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(71)出願人 000002886

大日本インキ化学工業株式会社  
東京都板橋区坂下3丁目35番58号

(72)発明者 鷹尾 長幸

茨城県竜ヶ崎市長ヶ丘3-8-19

(72)発明者 浅田 匡彦

千葉県佐倉市大崎台3-4-5-4-201

(72)発明者 齊藤 直人

千葉県四街道市美しが丘3-8-6 パー  
ディタウン6-A-202

(74)代理人 弁理士 高橋 勝利

(54)【発明の名称】 記録液用アニオン性マイクロカプセル化顔料含有水性分散液及び記録液

(57)【要約】

【課題】 水系の顔料分散液を用いた記録液の製造において、記録液の分散媒体に顔料を微細に分散する工程の省力化を実現することにより、多大な労力、設備、エネルギー等を省力化し記録液の製造コストの低減が可能で、さらに記録液用の樹脂、各種添加剤あるいは溶剤等の選択の自由度に優れた汎用性の高い記録液用の水性分散液を提供すること、さらに、記録液に要求される濃度感、高精細度、演色性や透明性、さらに耐水性等に優れた記録液用の水性分散液の提供及びその水性分散液を用いた記録液を提供すること。

【解決手段】 有機顔料又はカーボンブラックをアニオン性基含有有機高分子化合物類で被覆して成るアニオン性マイクロカプセル化顔料含有水性分散液であって、アニオン性マイクロカプセル化顔料中の有機顔料の含有割合が35～80重量%の範囲にある記録液用水性分散液。

## 【特許請求の範囲】

【請求項1】 有機顔料又はカーボンブラックをアニオン性基含有有機高分子化合物類で被覆して成るアニオン性マイクロカプセル化顔料含有水性分散液であって、アニオン性マイクロカプセル化顔料中の有機顔料又はカーボンブラックの含有割合が35～80重量%の範囲にあることを特徴とする記録液用水性分散液。

【請求項2】 アニオン性マイクロカプセル化顔料の最大粒子径が1000nm以下で、かつ平均粒子径が300nm以下である請求項1記載の記録液用水性分散液。

【請求項3】 最大粒子径が200nm以下で、かつ一次粒子の平均粒子径が10～100nmの範囲にある有機顔料又はカーボンブラックを含有するアニオン性マイクロカプセル化顔料であることを特徴とする請求項1又は2記載の記録液用水性分散液。

【請求項4】 硬化剤及び／又は高分子化合物と有機顔料とをアニオン性基含有有機高分子化合物類で被覆したアニオン性マイクロカプセル化顔料を含有することを特徴とする請求項1、2又は3記載の記録液用水性分散液。

【請求項5】 アニオン性基含有有機高分子化合物類が有機アミン塩である請求項1、2、3又は4記載の記録液用水性分散液。

【請求項6】 アニオン性基含有有機高分子化合物類がアルカリ金属塩である請求項1、2、3又は4記載の記録液用水性分散液。

【請求項7】 アニオン性基含有有機高分子化合物類の酸価が30KOHmg/g以上である請求項1、2、3、4、5又は6記載の記録液用水性分散液。

【請求項8】 アニオン性基がカルボキシル基である請求項7記載の記録液用水性分散液。

【請求項9】 アニオン性基含有有機高分子化合物類の数平均分子量が2000以上である請求項7又は8記載の記録液用水性分散液。

【請求項10】 アニオン性基含有有機高分子化合物類及び、有機顔料又はカーボンブラックを含有する有機溶剤相に水を投入することにより得られるアニオン性マイクロカプセル化顔料を用いる請求項1、2、3、5、6、7、8又は9記載の記録液用水性分散液。

【請求項11】 アニオン性基含有有機高分子化合物類、有機顔料又はカーボンブラック、及び硬化剤及び／又は高分子化合物を含有する有機溶剤相に水を投入することにより得られるアニオン性マイクロカプセル化顔料を用いる請求項4、5、6、7、8又は9記載の記録液用水性分散液。

【請求項12】 アニオン性基含有有機高分子化合物類及び、有機顔料又はカーボンブラックを含有する有機溶剤相に超音波を照射しながら水を投入することにより得られるアニオン性マイクロカプセル化顔料を用いる請求項10又は11記載の記録液用水性分散液。

【請求項13】 アニオン性基含有有機高分子化合物類及び、有機顔料又はカーボンブラックを含有する有機溶剤相を水中に投入することにより得られるアニオン性マイクロカプセル化顔料を用いる請求項1、2、3、5、6、7、8又は9記載の記録液用水性分散液。

【請求項14】 アニオン性基含有有機高分子化合物類、有機顔料又はカーボンブラック、及び硬化剤及び／又は高分子化合物を含有する有機溶剤相を水中に投入することにより得られるアニオン性マイクロカプセル化顔料を用いる請求項4、5、6、7、8又は9記載の記録液用水性分散液。

【請求項15】 アニオン性基含有有機高分子化合物類及び、有機顔料又はカーボンブラックからなる含水ケーキを、塩基性化合物を用いてアニオン性基の一部又はすべてを中和させることにより得られるアニオン性マイクロカプセル化顔料を用いる請求項1、2、3、4、5、6、7、8又は9記載の記録液用水性分散液。

【請求項16】 アニオン性基含有有機高分子化合物類のアニオン性基の一部又はすべてを塩基性化合物でもって中和し、有機顔料又はカーボンブラックと、水性媒体中で混練する工程、及び、酸性化合物でもってpHを中性又は酸性にしてアニオン性基含有有機高分子化合物類を析出させて顔料に固着する工程とからなる製法によって得られる含水ケーキを使用する請求項13又は14記載の記録液用水性分散液。

【請求項17】 請求項1、2、3、4、5、6、7、8、9、10、11、12、13、14、15又は16記載の記録液用水性分散液を含有する記録液。

【請求項18】 インクジェットプリンター用である請求項17記載の記録液。

## 【発明の詳細な説明】

## 【0001】

【発明の属する技術分野】本発明は、水性ボールペン、万年筆、水性サインペン、水性マーカー等の筆記具やバブルジェット方式、サーマルジェット方式やピエゾ方式等のオンデマンドタイプのインクジェットプリンター用の水性記録液を製造するための材料として有用なマイクロカプセル化顔料中の顔料濃度の高いアニオン性マイクロカプセル化顔料を含有する記録液用水性分散液、その分散液を含有する記録液に関する。

## 【0002】

【従来の技術】従来、高精細度を要求される記録液には染料が用いられてきた。染料を用いた記録液は、高透明度、高精細度や優れた演色性などの特徴を有しているが、耐光性及び耐水性等の問題を有する。

【0003】近年、耐光性及び耐水性の問題を解決するために、染料に代えて有機顔料やカーボンブラックを用いた記録液が製造されている。

【0004】しかしながら、有機顔料やカーボンブラックを用いた場合、顔料が非常に細かく分散安定化されて

いないと、記録液として高精細度と高度な演色性を得られないという問題点がある。特に、インクジェットプリンター用の記録液においては、顔料が非常に細かく分散安定化されていないと、ノズルの目詰まりという問題点に直結する。また、バックライトで投影する OHP シート等の用途に有機顔料を用いた場合、顔料を微細に分散して高透明度を確保しなければ、カラフルな OHP の投影画像が得られないという問題点があった。

【0005】特に、これらに使用される有機顔料やカーボンブラックは、塗料やインキ等の一般的に使用される有機顔料やカーボンブラックに比べて、一次粒子径が細かく、二次凝集が強いため、これらの顔料を一次粒子にまで分散するには多大なエネルギーを必要とする。また、これらの顔料を一次粒子まで分散できたとしても、分散液中の顔料を安定に保つには種々の工夫が必要である。

【0006】これらの問題点を解決するために、以下に示すように、マイクロカプセルを使用する方法が開示されている。例えば、特開昭 62-95366 号公報には、ポリマー粒子中に染料インクを内包したマイクロカプセルを記録液に用いる方法、特開平 1-170672 号公報には、水に実質的に不溶な溶媒に色素を溶解又は分散させ、これを水中で界面活性剤を用いて乳化分散し、従来の手法によりマイクロカプセル化した色素を記録液に用いる方法、特開平 5-39447 号公報には、マイクロカプセルの内包物が、水、水溶性溶媒並びにポリエステル樹脂の少なくとも 1 種に昇華性分散染料を溶解又は分散させたマイクロカプセルを記録組成物に使用する方法、特開平 6-313141 号公報等には着色された乳化重合粒子と種々の水性材料からなる水性インキ組成物等が開示されている。

【0007】

【発明が解決しようとする課題】しかしながら、染料をカプセル化したものの、耐光性に劣るという問題点を有し、従来の方法で製造したマイクロカプセル化顔料は、粒径が大きいために、透明性、発色性及び演色性に劣るという問題点を有していた。また、カプセル中の樹脂濃度が高い（顔料濃度が低い）ために、記録液に使用する材料の選択性が小さく、汎用性に欠け、さらにその記録液は、濃度感がなくなるという問題点を有していた。さらに、顔料濃度を過度に高めた場合、樹脂のみで微細なマイクロカプセル化顔料を製造することが難しく、それゆえに、界面活性剤を併用せざるを得ず、そのために、必ずしも耐水性を満足する記録画像が得られるものではなかった。

【0008】本発明が解決しようとする課題は、水系の顔料分散液を用いた記録液の製造において、記録液の分散媒体に顔料を微細に分散する工程の省力化を実現し、多大な労力、設備、エネルギー等を省力化し記録液の製造コストを低減可能なマイクロカプセル化顔料含有水性

分散液を提供すること、また、記録液用の樹脂、各種添加剤あるいは溶剤等の選択の自由度に優れた汎用性の高い記録液用のマイクロカプセル化顔料含有水性分散液を提供すること、さらに、記録液に要求される濃度感、高精細度、演色性や透明性、さらに耐水性や再分散性等に優れた記録液用のマイクロカプセル化顔料含有水性分散液と該水性分散液を用いた記録液を提供することにある。

【0009】

【課題を解決するための手段】本発明者らは、上記課題を解決すべく、鋭意、検討を重ねた結果、有機顔料又はカーボンブラックをアニオン性基含有有機高分子化合物類で被覆して成るアニオン性マイクロカプセル化顔料含有水性分散液であって、アニオン性マイクロカプセル化顔料中の有機顔料又はカーボンブラックの含有率が 35～80 重量%の範囲にあるアニオン性マイクロカプセル化顔料含有水性分散液を記録液に加工した場合、製造時の樹脂、溶剤あるいは各種添加剤等の選択や添加量の制限がなく、汎用性が高められ、更にアニオン性マイクロカプセル化顔料含有水性分散液を単に混合するだけで使用できるため、従来の製造コストを低減すること、記録液の精細度、演色性や透明性を従来以上に向上できること、界面活性剤を必須使用しなくても良いので、記録画像の耐水性を高めること、さらにマイクロカプセル化するための樹脂であるアニオン性基含有有機高分子化合物類の中和用の塩基を不揮発性のもの（アルカリ金属）を使用することにより再分散性を高め記録液の信頼性を高められること等を見出し、本発明を完成するに至った。

【0010】即ち、本発明は上記課題を解決するために、有機顔料又はカーボンブラックを、必要に応じて硬化剤及び高分子化合物と共に、アニオン性基含有有機高分子化合物類（以下、「アニオン性有機高分子化合物類」と省略する。）で被覆したアニオン性マイクロカプセル化顔料を含有する水性分散液であって、アニオン性マイクロカプセル化顔料中の有機顔料又はカーボンブラックの含有率が 35～80 重量%の範囲にあることを特徴とする記録液用アニオン性マイクロカプセル化顔料含有水性分散液及び該水性分散液を含有する記録液を提供する。

【0011】本発明のアニオン性マイクロカプセル化顔料を含有する記録液用水性分散液は、有機顔料又はカーボンブラックを、必要に応じて硬化剤及び高分子化合物と共に、アニオン性有機高分子化合物類で被覆したものであって、しかも、その有機顔料又はカーボンブラックの含有量が 35～80 重量%で、有機顔料又はカーボンブラックの一次粒子の最大粒子径が 200 nm 以下であって平均粒子径が 10～100 nm の範囲にあり、かつアニオン性マイクロカプセル化顔料の最大粒子径が 1000 nm 以下でかつ平均粒子径が 300 nm 以下であるものが特に好ましい。また、アニオン性有機高分子化合

物類を塩基で中和した形の方が好ましく、特にアルカリ金属を使用することが好ましい。

【0012】更に、そのアニオン性マイクロカプセル化顔料が、硬化剤及び高分子化合物を含有するアニオン性有機高分子化合物類で以て、有機顔料を被覆した形のものであれば、一層、好ましい。

【0013】更にまた、本発明のマイクロカプセル化顔料のカプセル中に、チタン、アルミの如き無機物質、顔料誘導体、顔料分散剤、顔料湿潤剤、有機溶剤、可塑剤、紫外線吸収剤、酸化防止剤、あるいは記録液用のビヒクル等の他の物質を含めることもできる。

【0014】

【発明の実施の形態】本発明の記録液用水性分散液に含まれるアニオン性マイクロカプセル化顔料の製造方法としては、従来からの方法として物理的、機械的手法と、コアセルベーション法、界面重合法及びイン・サイチュール法などの化学的手法との、二つの方法が挙げられる。

【0015】しかしながら、これらの従来型方法で得られるマイクロカプセル化顔料の粒径は、サブミクロン( $\mu\text{m}$ )以下の大きさのものであっても、粒子径が大きく、マイクロカプセル中の顔料が占める割合が低い場合、このマイクロカプセル化顔料を用いて記録液を製造した場合、精細度、演色性、透明性あるいは色の濃度感において必ずしも満足できるものが得られない。更に微細で、かつ、マイクロカプセル中の顔料が占める割合が高いマイクロカプセル化顔料を製造する必要がある。

【0016】また、カプセル中の樹脂濃度が高い(顔料濃度が低い)ために、記録液に使用する材料が限られたり、界面活性剤を使用するために耐水性が劣ったりする。

【0017】本発明の記録液用水性分散液に含まれるアニオン性マイクロカプセル化顔料の製造方法としては、基本的には、水に対して自己分散能又は溶解能を有するアニオン性有機高分子化合物類と有機顔料又はカーボンブラックとの混合物(複合物ないしは複合体)を、あるいは有機顔料又はカーボンブラックと硬化剤及びアニオン性有機高分子化合物との混合物を有機溶媒相とし、該有機溶媒相に水を投入するか、あるいは、水中に該有機溶媒相を投入して、自己分散(転相乳化)化する方法(以下、「転相法」という。)が好ましい。

【0018】あるいは、アニオン性基含有有機高分子化合物類のアニオン性基の一部又はすべてを塩基性化合物でもって中和し、有機顔料又はカーボンブラックと、水性媒体中で混練する工程、及び、酸性化合物でもってpHを中性又は酸性にしてアニオン性基含有有機高分子化合物類を析出させて顔料に固着する工程とからなる製法によって得られる含水ケーキを、塩基性化合物を用いてアニオン性基の一部又はすべてを中和させることにより得る方法(以下、「酸析法」という。)も好ましい。

【0019】このようにすることによって、目的とする

従来の方法より微細で高顔料分のアニオン性マイクロカプセル化顔料を含有する水性分散液を製造することができる。

【0020】また、上記転相法において、有機溶媒相中に、記録液用のビヒクルや添加剤を混入させて製造しても何等問題はない。特に、直接記録液用の分散液を製造できることから言えば、記録液用のビヒクルを混入させる方がより好ましい。

【0021】アニオン性マイクロカプセル化顔料のマイクロカプセル中に含まれる有機顔料又はカーボンブラックは、記録液の濃度感や透明性、演色性を得るために、あるいは、平均粒子径300nm以下の微細なマイクロカプセル化顔料を製造するために、最大粒子径が200nm以下であって、一次粒子の平均粒子径が10~100nmの範囲にある有機顔料又はカーボンブラックが好ましい。

【0022】本発明で使用する有機顔料の種類は特に限定されないが、代表的なものを例示するととどめれば、キナクリドン系顔料、キナクリドンキノ系顔料、ジオキサジン系顔料、フタロシアニン系顔料、アントラピリミジン系顔料、アンサンスロン系顔料、インダンスロン系顔料、フラバンスロン系顔料、ペリレン系顔料、ジケトピロロピロール系顔料、ペリノン系顔料、キノフタロン系顔料、アントラキノ系顔料、チオインジゴ系顔料、ベンツイミダゾロン系顔料、イソインドリノン系顔料、アゾメチン系顔料又はアゾ系顔料などが挙げられる。

【0023】また、カーボンブラックは、中性、酸性、塩基性カーボン等が挙げられる。

【0024】アニオン性マイクロカプセル化顔料のマイクロカプセル中に顔料と共に含まれていても良い硬化剤としては、例えば、メラミン樹脂、ベンゾグアナミン樹脂、尿素樹脂等のアミノ樹脂、トリメチロールフェノール、その縮合物等のフェノール樹脂、テトラメチレンジイソシアネート(TDI)、ジフェニルメタンジイソシアネート(MDI)、ヘキサメチレンジイソシアネート(HDI)、ナフタレンジイソシアネート(NDI)、イソホロンジイソシアネート(IPDI)、キシリレンジイソシアネート(XDI)、それらの変性イソシアネートやブロックダイイソシアネート等のポリイソシアネート、脂肪族アミン、芳香族アミン、N-メチルピペラジン、トリエタノールアミン、モルホリン、ジアルキルアミノエタノール、ベンジルジメチルアミン等のアミン類、ポリカルボン酸、無水フタル酸、無水マレイン酸、無水ヘキサヒドロフタル酸、無水ピロメリット酸、無水ベンゾフェノンテトラカルボン酸、エチレングリコールビストリメリテート等の酸無水物、ビスフェノールA型エポキシ樹脂、フェノール系エポキシ樹脂、グリシジルメタクリレート共重合体、カルボン酸のグリシジルエステル樹脂、脂環式エポキシ等のエポキシ化合物、ポリエ



ーテルポリオール、ポリブタジエングリコール、ポリカプロラクトンポリオール、トリスヒドロキシエチルイソシアネート (THEIC) 等のアルコール類、ペルオキシドによるラジカル硬化あるいはUV硬化や電子線硬化に用いる不飽和基含有化合物としてのポリビニル化合物、ポリアリル化合物、グリコールやポリオールとアクリル酸又はメタクリル酸の反応物等のビニル化合物等が挙げられる。

【0025】これらの硬化剤は、アニオン性マイクロカプセル化顔料の壁を硬化するために、あるいは、記録液に使用した場合の塗膜強度を高めるために使用され、更に必要であれば、光開始剤、重合開始剤あるいは触媒を添加し、硬化の促進を図るのがより好ましい。

【0026】そのような目的で使用する光開始剤としては、ベンゾイン類、アントラキノン類、ベンゾフェノン類、含イオウ化合物類やジメチルベンジルケタール等が挙げられるが、これらに限定される物ではない。

【0027】同様に、重合開始剤としては、例えば、 $t$ -ブチルパーオキシベンゾエート、ジ- $t$ -ブチルパーオキシド、クメンパーヒドロキシド、アセチルパーオキシド、ベンゾイルパーオキシド、ラウロイルパーオキシド等の如き過酸化化合物；アゾビスイソブチルニトリル、アゾビス-2, 4-ジメチルバレロニトリル、アゾビスシクロヘキサンカルボニトリル等の如きアゾ化合物などが挙げられる。

【0028】また同様に、触媒としては、例えば、Co化合物、Pb化合物などが挙げられる。

【0029】アニオン性マイクロカプセル化顔料のマイクロカプセル中に顔料と共に含まれていても良い高分子化合物は、数平均分子量1, 000以上のものであれば、特に制限なく使用することができるが、記録液の膜強度の面、カプセルの製造面から、数平均分子量が3, 000~100, 000の範囲のものが好ましい。

【0030】そのような高分子化合物の種類は特に限定されないが、例えば、塩化ビニル、酢酸ビニル、ポリビニルアルコール、ポリビニルブチラール等のポリビニル系、アルキド樹脂、フタル酸樹脂等のポリエステル系、メラミン樹脂、メラミンホルムアルデヒド樹脂、アミノアルキド共縮合樹脂、ユリア樹脂、尿素樹脂等のアミノ系、熱可塑性、熱硬化性あるいは変性のアクリル系、エポキシ系、ポリウレタン系、ポリエーテル系、ポリアミド系、不飽和ポリエステル系、フェノール系、シリコン系、フッ素系等の高分子化合物、あるいはそれらの共重合体又は混合物などが挙げられる。

【0031】アニオン性マイクロカプセル化顔料を製造するために使用するアニオン性有機高分子化合物類は、水に対して自己分散能又は溶解能を有し、アニオン性（酸性）であれば特に制限がないが、カプセル膜として、あるいは記録液の塗膜として充分なるものを得るために、通常、数平均分子量が1, 000~100, 00

0の範囲のものが好ましく、3, 000~50, 000の範囲のものが特に好ましく、かつ、有機溶剤に溶解して溶液となるものが好ましい。

【0032】アニオン性有機高分子化合物類それ自体の自己分散能あるいは溶解能は、特に限定されないが、例えば、当該アニオン性有機高分子化合物中のカルボキシル基、スルホン酸基やホスホン酸基の如きアニオン性基を、アンモニアやトリエチルアミンの如き有機アミンや水酸化ナトリウム、水酸化カリウムや水酸化リチウム等のアルカリ金属を用いて中和することによって付与される。特に望ましい自己分散能又は溶解能は、この有機高分子化合物類中に、カルボキシル基を導入せしめて、塩基で以て中和せしめるという形のものである。アニオン性有機高分子化合物類中には、これらのアニオン性基を2種以上有していても良い。

【0033】カルボキシル基を有するアニオン性高分子化合物類中のカルボキシル基の量は、酸価が30KOHmg/g以上が好ましく、50~250となる範囲がより好ましい。アニオン性高分子化合物類の酸価が250を越えると、親水性が高くなり過ぎるため、カプセルの貯蔵安定性が損なわれたり記録画像の耐水性が著しく低下する傾向にあり、また、酸価が30よりも低いと、カプセルの安定性が損なわれたり粒子径が大きくなる傾向にあるので、好ましくない。

【0034】そのようなアニオン性有機高分子化合物類としては、例えば、塩化ビニル、酢酸ビニル、ポリビニルアルコール、ポリビニルブチラール等のポリビニル系、アルキド樹脂、フタル酸樹脂等のポリエステル系、メラミン樹脂、メラミンホルムアルデヒド樹脂、アミノアルキド共縮合樹脂、ユリア樹脂、尿素樹脂等のアミノ系の材料；熱可塑性、熱硬化性あるいは変性のアクリル系、エポキシ系、ポリウレタン系、ポリエーテル系、ポリアミド系、不飽和ポリエステル系、フェノール系、シリコン系、フッ素系高分子化合物、あるいはそれらの共重合体又は混合物などのアニオン性基を有する材料などが挙げられる。

【0035】本発明で使用するアニオン性有機高分子化合物類は、カプセル壁材として充分なる分子量を有し、特に壁形成化という操作を必要としないが、カプセル壁の耐溶剤性や耐久性などの特性を一層向上化させるために、あるいは、記録液の膜形成後の膜強度を高めるために、予め、使用するアニオン性有機高分子化合物類それ自体に、グリシジル基、イソシアネート基、水酸基又は $\alpha$ ,  $\beta$ -エチレン性不飽和二重結合（ビニル基）の如き反応性活性基をペンダントさせておくことによって、あるいは、反応性活性基を有する架橋剤、例えば、メラミン樹脂、ウレタン樹脂エポキシ樹脂、エチレン性不飽和モノマーやオリゴマー等の光硬化剤などを混入させておくことによって、カプセルの形成時又は形成後、あるいは、記録液の塗膜形成後に、これらの反応性活性基や官

能基などを利用して、カプセル壁材用としてのアニオン性有機高分子化合物類それ自体の分子量を増大化させたり、架橋しゲル化する性能を付与させておくことがより好ましい。

【0036】アニオン性有機高分子化合物類のうち、アニオン性アクリル系樹脂は、例えば、アニオン性基を有するアクリルモノマー（以下、アニオン基含有アクリルモノマーと略す）と、更に必要に応じてこれらのモノマーと共重合し得る他のモノマーを溶媒中で重合して得られる。アニオン基含有アクリルモノマーとしては、例えば、カルボキシ基、スルホン酸基、ホスホン基からなる群から選ばれる1個以上のアニオン性基を含むアクリルモノマーが挙げられ、これらの中でもカルボキシ基を有するアクリルモノマーが特に好ましい。

【0037】カルボキシ基を有するアクリルモノマーとしては、例えば、アクリル酸、メタクリル酸、クロトン酸、エタアクリル酸、プロピルアクリル酸、イソプロピルアクリル酸、イタコン酸、フマル酸等が挙げられる。これらの中でもアクリル酸及びメタクリル酸が好ましい。

【0038】スルホン酸基を有するアクリルモノマーとしては、例えば、スルホエチルメタクリレート、ブチルアクリルアミドスルホン酸等が挙げられる。

【0039】ホスホン基を有するアクリルモノマーとしては、例えば、ホスホエチルメタクリレート等が挙げられる。

【0040】アニオン基含有アクリルモノマーと共重合し得る他のモノマーとしては、例えば、アクリル酸メチル、アクリル酸エチル、アクリル酸イソプロピル、アクリル酸-*n*-プロピル、アクリル酸-*n*-ブチル、アクリル酸-*t*-ブチル、アクリル酸-2-エチルヘキシル、アクリル酸-*n*-オクチル、アクリル酸ラウリル、アクリル酸ベンジル、メタクリル酸メチル、メタクリル酸エチル、メタクリル酸イソプロピル、メタクリル酸-*n*-プロピル、メタクリル酸-*n*-ブチル、メタクリル酸イソブチル、メタクリル酸-*t*-ブチル、メタクリル酸-2-エチルヘキシル、メタクリル酸-*n*-オクチル、メタクリル酸ラウリル、メタクリル酸ステアリル、メタクリル酸トリデシル、メタクリル酸ベンジル等の如き（メタ）アクリル酸エステル；ステアリン酸とグリシジルメタクリレートの付加反応物等の如き脂肪酸とオキシラン構造を有する（メタ）アクリル酸エステルモノマーとの付加反応物；炭素原子数3以上のアルキル基を含むオキシラン化合物と（メタ）アクリル酸との付加反応物；スチレン、 $\alpha$ -メチルスチレン、*o*-メチルスチレン、*m*-メチルスチレン、*p*-メチルスチレン、*tert*-ブチルスチレン等の如きスチレン系モノマー；イタコン酸ベンジル等の如きイタコン酸エステル；マレイン酸ジメチル等の如きマレイン酸エステル；フマル酸ジメチル等の如きフマル酸エステル；アクリロ

ニトリル、メタクリロニトリル、酢酸ビニル、アクリル酸イソボルニル、メタクリル酸イソボルニル、アクリル酸アミノエチル、アクリル酸アミノプロピル、アクリル酸メチルアミノエチル、アクリル酸メチルアミノプロピル、アクリル酸エチルアミノエチル、アクリル酸エチルアミノプロピル、アクリル酸アミノエチルアミド、アクリル酸アミノプロピルアミド、アクリル酸メチルアミノエチルアミド、アクリル酸メチルアミノプロピルアミド、アクリル酸エチルアミノエチルアミド、アクリル酸エチルアミノプロピルアミド、メタクリル酸アミド、メタクリル酸アミノエチル、メタクリル酸アミノプロピル、メタクリル酸メチルアミノエチル、メタクリル酸メチルアミノプロピル、メタクリル酸エチルアミノエチル、メタクリル酸エチルアミノプロピル、メタクリル酸アミノエチルアミド、メタクリル酸アミノプロピルアミド、メタクリル酸メチルアミノエチルアミド、メタクリル酸メチルアミノプロピルアミド、メタクリル酸エチルアミノエチルアミド、メタクリル酸エチルアミノプロピルアミド、アクリル酸ヒドロキシメチル、アクリル酸-2-ヒドロキシエチル、アクリル酸-2-ヒドロキシプロピル、メタクリル酸ヒドロキシメチル、メタクリル酸-2-ヒドロキシエチル、メタクリル酸-2-ヒドロキシプロピル、*N*-メチロールアクリルアミド、アリールアルコール等が挙げられる。

【0041】架橋性官能基を有するモノマーとしては、下記に挙げられる。

【0042】ブロックイソシアネート基を有する重合性モノマーは、2-メタクリロイルオキシエチルイソシアネートなどのイソシアネート基を有する重合性モノマーに公知のブロック剤を付加反応させることによって、あるいは、上述した水酸基およびカルボキシ基を有するビニル系共重合体に、イソシアネート基とブロックイソシアネート基とを有する化合物を付加反応することによって、容易に製造することができる。イソシアネート基とブロックイソシアネート基とを有する化合物は、ジイソシアネート化合物と公知のブロック剤とをモル比で約1:1の割合で付加反応させることによって容易に得ることができる。

【0043】エポキシ基を有するモノマーとしては、例えば、グリシジル（メタ）アクリレート、脂環式エポキシ基を有する（メタ）アクリレートモノマーなどが挙げられる。

【0044】1, 3-ジオキソラン-2-オン-4-イル基を有するモノマーとしては、例えば、1, 3-ジオキソラン-2-オン-4-イルメチル（メタ）アクリレート、1, 3-ジオキソラン-2-オン-4-イルメチルビニルエーテルなどが挙げられる。

【0045】重合開始剤としては、例えば、*t*-ブチルパーオキシベンゾエート、ジ-*t*-ブチルパーオキシド、クメンパーヒドロキシド、アセチルパーオキシド、

ベンゾイルパーオキシド、ラウロイルパーオキシド等の如き過酸化物；アゾビスイソブチルニトリル、アゾビス-2, 4-ジメチルバレロニトリル、アゾビスシクロヘキサンカルボニトリル等の如きアゾ化合物などが挙げられる。

【0046】アニオン性基含有アクリルモノマーと、更に必要に応じて、これらのモノマーと共重合し得る他のモノマーを重合する際に使用する溶媒としては、例えば、ヘキサン、ミネラルスピリット等の如き脂肪族炭化水素系溶剤；ベンゼン、トルエン、キシレン等の如き芳香族炭化水素系溶剤；酢酸ブチル等の如きエステル系溶剤；メチルエチルケトン、イソブチルメチルケトン等の如きケトン系溶剤；メタノール、エタノール、ブタノール、イソプロピルアルコール等の如きアルコール系溶剤；ジメチルホルムアミド、ジメチルスルホキシド、N-メチルピロリドン、ピリジン等の如き非プロトン性極性溶剤などが挙げられる。これらの溶剤は2種以上を併用して用いることもできる。

【0047】転相法によるアニオン性マイクロカプセル化顔料含有水性分散液は、以下のようにして製造される。

【0048】転相法において、水に対して自己分散能又は溶解能を有するアニオン性有機高分子化合物類と有機顔料又はカーボンブラックとの混合物（複合物ないしは複合体）、あるいは有機顔料又はカーボンブラックと硬化剤及びアニオン性有機高分子化合物との混合物を有機溶媒相とする際に用いる有機溶剤は、特に限定されるものではなく、アニオン性有機高分子化合物類を溶解し得るものである限り、いずれのものも使用できるが、製造時の溶剤除去の容易さの面から、アセトン、メチルエチルケトンの如きケトン系溶剤；酢酸エチルの如きエステル系溶剤；エタノール、イソプロピルアルコールの如きアルコール系溶剤；ベンゼンの如き芳香族炭化水素系溶剤などの低沸点の溶剤が好ましい。

【0049】アニオン性有機高分子化合物類の割合は、有機顔料又はカーボンブラックの100重量部に対して、25～186重量部の範囲が好ましく、30～150重量部の範囲が特に好ましい。

【0050】特に、有機相である混合物（複合物ないしは複合体）にとって望ましいことは、顔料が有機高分子化合物類中に微細に、かつ、均一に、何ら凝集することなく、分散安定化されていると同時に、架橋剤や高分子化合物が、アニオン性有機高分子化合物類中に相溶しているということであるが、決して、これのみに限定されるものではない。

【0051】かかる混合物の分散安定化法としては、特に限定されるものではないが、それらのうちでも特に代表的なもののみを例示するにとどめれば、(1) 粉末有機顔料又はカーボンブラックを、ビーズミル、ロールミルやサンドミルなどのような、種々の分散機を用いて、

アニオン性有機高分子化合物類中に微分散化せしめ、次いで、硬化剤や高分子化合物などを、溶解ないしは分散化せしめるというような方法、あるいは、(2) 有機顔料の合成後のウェット・ケーキ又はカーボンブラックのウェットケーキ、即ち、水に顔料を分散化せしめたままの状態のものを、中和前のアニオン性有機高分子化合物類中に、ニーダーなどの種々の分散機を用いて、フラッシングせしめることによって微分散化せしめ、次いで、硬化剤や高分子化合物なども、溶解ないしは分散化せしめるというような方法、などが挙げられる。これらの分散方法において、超微粒子を得るためには、ビーズミル分散あるいはフラッシングする方法がより好ましい。

【0052】また、特に後者の方法は、ウェット・ケーキを用いるので、有機顔料類の乾燥工程を必要としないために、省エネルギーになり、しかも、乾燥工程中に起こる強固なる凝集も、全く起こらないので、極めて有用性の高いものである。

【0053】さらに、分散安定化を目的として、ジアルキルアミノメチル基やスフオンサン基、スフオンアミド基、フタルイミド基等を有する顔料誘導体；ビッグケミー社製の「BYK-160」、「BYK-166」、ゼネカ社製の「ソルスパーズ24000」等の顔料分散剤等を使用して、分散時間等を短縮させることもできる。

【0054】自己分散（転相乳化）を容易にするために、また、溶剤除去操作を簡便にするために混合物中の溶剤の使用量はできるだけ低く抑えることが望ましく、そのような面から、これらの混合物の粘度は、10000CP以下に調製することが望ましい。

【0055】混合物の有機相に水を投入することによって、あるいは、水中に該有機相を投入することによって、自己分散（転相乳化）させるが、その方法としては、有機相又は水のいずれか一方を、適度に攪拌しながら、その中へ、他方を、ゆっくりと投入することによって、瞬時に、目的とするマイクロカプセル化顔料を形成することができる。

【0056】こうした攪拌における、攪拌機の種類や速度などは、形成される粒子の大きさには、余り、影響を及ぼさないので、攪拌機の種類や攪拌速度は特に制限されない。

【0057】このような製法において、上記の手順のもので十分微細なマイクロカプセル化顔料を作ることが可能であるが、更に微細なものを作る方法としては、超音波を有機相にあてながら転相乳化させることである。その超音波の周波数は、特に限定されないが、好ましくは10～200KHzである。

【0058】いわゆる中和型のアニオン性有機高分子化合物類を使用する際には、中和用の塩基類を、予め、必要量だけ、有機相あるいは水相に溶解せしめておく必要がある。特に、有機相での顔料の凝集を考慮して、水相に塩基類を溶解させておくことがより好ましい。

【0059】また、形成されたカプセル壁をゲル化処理するために、あるいは、記録液の膜形成後の膜強度を高めるために用いられる架橋剤は、例えば、ポリアミン類の如き水溶性の化合物を用いる場合であっても、予め、必要量だけ、有機相に溶解しておく必要がある。

【0060】これらの種々の方法で得られるアニオン性マイクロカプセル化顔料含有水性分散液は、実用に供される形態によって、そのまま使用することもでき、あるいは脱溶剤を行なって水性分散体として使用することもできる。

【0061】脱溶剤を行なう方法としては、一般的なる蒸留法や減圧蒸留法などが挙げられる。

【0062】一方、上記と同様の材料を使用して、アニオン性基含有有機高分子化合物類及び有機顔料又はカーボンブラックからなる含水ケーキを、塩基性化合物を用いてアニオン性基の一部又はすべてを中和させることにより、アニオン性マイクロカプセル化顔料含有水性分散液を得る方法（酸析法）は、以下の手順による。

(1) アニオン性有機高分子化合物類と顔料とを、アルカリ性水性媒体中に分散する。また、必要に応じて加熱処理を行ない、樹脂のゲル化を図る。

(2) pHを中性又は酸性にすることによって樹脂を疎水化し、樹脂を顔料に強く固着する。

(4) 必要に応じて、濾過及び水洗を行なう。

(5) 塩基性化合物でもってカルボキシル基を中和して、水性媒体中に再分散する。また、必要に応じて加熱処理を行ない、樹脂のゲル化を図る。

【0063】工程(1)におけるアニオン性有機高分子化合物類と顔料とを、アルカリ性水性媒体中に分散する方法としては、次の2方法が適当である。

(1) 有機溶剤媒体中で顔料を混練した後、水性媒体中に分散する。

(2) 水性媒体中で顔料を混合又は混練する。

【0064】上記第(1)の方法では、まず、顔料と、アニオン性有機高分子化合物類の有機溶剤溶液とを、ボールミル、サンドミル、コロイドミルなどの公知の分散機を使用して微細に分散する。

【0065】この時、使用される有機溶剤は、一般に使用されるものはすべて使用できるが、樹脂に対する溶解性が良く、樹脂の合成上も問題がないもの、蒸気圧が水より高く、脱溶剤し易いもの、さらに、水と混和性のあるものが好ましい。そのような溶剤としては、例えば、アセトン、メチルエチルケトン、メタノール、エタノール、n-プロパノール、イソプロパノール、酢酸エチル、テトラヒドロフランなどが挙げられる。水との混和性は低いが、メチルイソプロピルケトン、メチル-n-プロピルケトン、酢酸イソプロピル、酢酸n-プロピル、塩化メチレン、ベンゼンなども、この方法に使用することができる。

【0066】有機溶剤媒体中に分散させた顔料及びアニ

オン性有機高分子化合物類から成る分散体を水性媒体中に分散させるには、(1) アニオン性有機高分子化合物類のカルボキシル基を塩基性化合物を用いて中和し、アニオン性有機高分子化合物類を親水性化して水に分散させる方法、あるいは、(2) 塩基性化合物を用いて中和したアニオン性有機高分子化合物類及び顔料から成る分散体を水に分散させる方法が挙げられる。

【0067】水への分散方法としては、次のような方法が適当である。

(a) アニオン性有機高分子化合物類及び顔料から成る分散体を塩基性化合物を用いて中和した後、水を滴下する。

(b) 塩基性化合物を用いて中和したアニオン性有機高分子化合物類及び顔料から成る分散体に、水を滴下する。

(c) アニオン性有機高分子化合物類及び顔料から成る分散体に、塩基性化合物を含有する水を滴下する。

(d) アニオン性有機高分子化合物類及び顔料から成る分散体を塩基性化合物でもって中和し、水媒体中に添加する。

(e) 塩基性化合物を用いて中和したアニオン性有機高分子化合物類及び顔料から成る分散体を水性媒体中に添加する。

(f) アニオン性有機高分子化合物類及び顔料から成る分散体を、塩基性化合物を含有する水媒体中に添加する。

【0068】水に分散する時には、通常の低シェアーでの攪拌、ホモナイザーなどでの高シェアー攪拌、あるいは、超音波などを使用して行なってもよい。また、水性媒体への分散を補助する目的でもって、界面活性剤や保護コロイドなどを、塗膜の耐水性を著しく低下させない範囲で併用することもできる。

【0069】塩基性化合物としては、例えば、水酸化ナトリウム、水酸化カリウム、水酸化リチウムの如きアルカリ金属；アンモニア、トリエチルアミン、トリブチルアミン、ジメチルエタノールアミン、ジイソプロパノールアミン、モルホリンの如き有機アミンなどが挙げられる。

【0070】アニオン性有機高分子化合物類と顔料とをアルカリ性水性媒体中に分散する第(1)工程に適用できる第(2)の方法である水性媒体中で樹脂と顔料とを混練する方法は、まず、アニオン性有機高分子化合物類のカルボキシル基を前記した塩基性化合物を用いて中和し、水性媒体中で顔料と混合又は混練する。この時、水に溶解又は分散した樹脂が、有機溶剤を含有していても差し支えないし、脱溶剤を行なって実質的に水のみの媒体であってもよい。顔料は、粉末顔料、水性スラリー、プレスケーキのいずれも使用できる。水性媒体中で分散する場合においては、顔料は、製造工程を簡略化するために、顔料粒子の2次凝集の少ない水性スラリー又はブ

レスケーキを使用することが好ましい。混練方法、有機溶剤、塩基性化合物は、有機溶剤媒体中での分散の場合と同じ方法、同じ材料が使用可能である。

【0071】有機溶剤系、水性系いずれの混練の場合であっても、顔料の分散を補助する目的のために、記録画像の耐水性を低下させない範囲で、顔料分散剤や湿潤剤を使用することもできる。

【0072】また、顔料を混練する際、あるいは、混練後であって酸析する前に、顔料以外の物質、例えば、染料、酸化防止剤、紫外線吸収剤、被覆剤バインダーの硬化触媒、防錆剤、香料、薬剤などを添加することもできる。

【0073】アニオン性有機高分子化合物類の使用割合は、有機顔料の100重量部に対して、25～186重量部、好ましくは30～150重量部なる範囲内が適切である。アニオン性有機高分子化合物類の使用割合が25重量部よりも少ない場合、顔料を充分微細に分散しにくくなる傾向にあり、また、186重量部よりも多い場合、分散体中の顔料の割合が少なくなり、水性顔料分散体を記録液に使用した時に、配合設計上の余裕がなくなる傾向にあるので、好ましくない。

【0074】さらに、顔料を混練した後、加熱処理により、アニオン性有機高分子化合物類のゲル化を図る場合、混練後の分散液の不揮発分を15%以下、好ましくは10%以下で行なうことが好ましい。

【0075】また、加熱温度は樹脂の架橋が進む温度以上であれば何等問題はないが、好ましい温度範囲は、70℃～200℃である。加熱温度が70℃未満では、架橋時間がかかりすぎ、加熱温度が200℃を越えると、顔料の種類によっては、結晶成長したり分散安定性が壊れたりして、カプセル化しにくい傾向にあるので好ましくない。

【0076】水性媒体中に微分散された顔料に樹脂を強く固着化する目的で行なわれる酸析は、塩基性化合物によって中和されたアニオン性有機高分子化合物類のカルボキシル基を、酸性化合物を加えてpHを中性又は酸性とすることによって、樹脂を疎水性化するものである。

【0077】使用される酸性化合物としては、例えば、塩酸、硫酸、磷酸、硝酸の如き無機酸類；蟻酸、酢酸、プロピオン酸の如き有機酸類などが使用できるが、排水中の有機物が少なく、かつ、酸析効果も大きい塩酸あるいは硫酸が好ましい。酸析時のpHは2～6の範囲が好ましいが、顔料によっては酸によって分解されるものもあり、このような顔料の場合には、pH4～7の範囲で酸析することが好ましい。酸析を行なう前に、系に存在する有機溶剤を減圧蒸留などの方法を用いて予め除しておくことが好ましい。

【0078】酸析後、必要に応じて濾過及び水洗を行なって、分散顔料の含水ケーキを得る。濾過方法としては、吸引濾過、加圧濾過、遠心分離など公知の方法が採

用できる。

【0079】この含水ケーキは、乾燥させることなく、含水した状態のまま塩基性化合物でもってカルボキシル基を再中和することによって、顔料粒子が凝集することなく、微細な状態を保持したままで、水性媒体中に再分散される。塩基性化合物としては、記録液の再分散性や耐水性を考慮し、水酸化ナトリウム、水酸化カリウム、水酸化リチウム等のアルカリ金属やトリエタノールアミン、ジエタノールアミン等の揮発しにくい有機アミン化合物等の単独、あるいは、これらと、アンモニア、トリエチルアミン、ジメチルエタノールアミンの如き揮発性アミン化合物との併用が好ましい。

【0080】このように、本発明で使用するアニオン性マイクロカプセル化顔料は、何ら、乳化剤などのような、いわゆる補助材料を使用せずとも、微小粒子のカプセル化が可能であり、極めて簡便にして、微小カプセルを調製することができる。

【0081】本発明で使用するマイクロカプセル化顔料中の有機顔料の平均粒子径は、電子顕微鏡で撮影した写真を用いて、数十サンプルの顔料の長径と短径を加えて平均した実測値を用いる。

【0082】本発明で使用するマイクロカプセル化顔料の平均粒子径は、粒子径測定方法によって多少違いがでることから電子顕微鏡で測定した実測値を用いることが好ましいが、レーザードップラー方式の粒子径測定装置を用いて測定することもできる。

【0083】このようにして得られるアニオン性マイクロカプセル化顔料含有水性分散液は、顔料の分散安定性が従来以上に改善され、記録液の色材として使用することにより、記録液の精細度や耐光性、演色性、透明性等の性能が向上するという利点がある。また、マイクロカプセル中の顔料濃度が高いことから、汎用性が高く、顔料を分散する工程の省力化ができるので、分散エネルギーと労力の省力化が図れるという利点もある。また、界面活性剤等を使用しないため耐水性も向上される。さらに、従来使用できなかった油性の硬化剤や記録液用ビヒクルをマイクロカプセル化顔料のカプセル中に含ませることができるので、使用できる材料の幅が広がり、直接記録液を製造することもできる。

【0084】請求項1で規定したように、アニオン性マイクロカプセル化顔料中の有機顔料の含有率は35～80重量%の範囲が好ましい。アニオン性マイクロカプセル化顔料中の有機顔料の含有率が35%よりも少ない場合、カプセル中の樹脂濃度が高くなるために、記録液用の樹脂や溶剤、助剤等の添加剤と相溶性が限られることがあったり、その添加剤等の添加量が制限されたりするために汎用性に欠け、さらに、カプセル中の顔料濃度が低くなるため、記録液としての水性分散液として使用した場合は、色濃度が高められなかったり、色濃度を高めるために記録液中のマイクロカプセル化顔料の使用割合



を高くせざるを得なくなる結果、記録液の粘度が高くなる傾向にあるので好ましくない。また、アニオン性マイクロカプセル化顔料中の有機顔料の含有率が80重量%よりも多い場合、有機顔料を微細に分散し難くなる傾向にあるので好ましくない。

【0085】また、アニオン性マイクロカプセル化顔料の最大粒子径が1000nmより大きくなった場合、ジェットインキプリンターのノズルを目詰まりさせることもあり、請求項2で規定したように、アニオン性マイクロカプセル化顔料の最大粒子径は1000nm以下で、500nm以下であるものがより好ましい。

【0086】さらに、そのアニオン性マイクロカプセル化顔料中の有機顔料の平均粒子径は300nm以下が好ましく、250nm以下が特に好ましい。使用する有機顔料の平均粒子径が300nmより大きくなると、分散液中のマイクロカプセル化顔料が長期に保存した場合、沈降したり、マイクロカプセル化の際に顔料が凝集した状態でカプセル化されるため、記録液として使用した場合、発色性や透明性あるいは精細度が劣り、特に、OHPシート等に記録した場合、光の透過を遮り、きれいな色を映し出せない傾向にあるので好ましくない。

【0087】本発明のアニオン性マイクロカプセル化顔料中のアニオン性有機高分子化合物類は、アルカリ金属や有機アミンの塩の形で使用されることが好ましい。水酸化ナトリウム、水酸化カリウム、水酸化リチウム等のアルカリ金属の塩の形で使用した場合、記録画像中に無機塩基が残存するために、その記録画像の耐水性が悪くなる傾向にあるが、再分散性に優れ記録液の信頼性が高くなることから好ましい。

【0088】上記有機アミンとしては、例えば、アンモニア、トリエチルアミン、トリブチルアミン、ジメチルエタノールアミン、ジイソプロパノールアミン、モルホリンの如き揮発性アミン化合物；ジエタノールアミン、トリエタノールアミン等の揮発しにくい高沸点の有機アミン等が挙げられる。

【0089】本発明の記録液用アニオン性マイクロカプセル化顔料含有水性分散液に含まれるアニオン性マイクロカプセル化顔料の含有量は、水性分散液100重量部中に、70重量部以下が好ましく、2～60重量部の範囲がより好ましく、10～50重量部の範囲が特に好ましい。水性分散液中のマイクロカプセル化顔料の含有量が70重量部より高くなると、実質的には水性分散液が固形状を呈する傾向にあるため、マイクロカプセルの凝集が起こり再度分散を必要とするため、好ましくない。また、水性分散液中のマイクロカプセル化顔料の含有量が2重量部よりも少なくなると、記録液に使用した場合、色濃度が十分得られない傾向にあるので好ましくない。記録液に、その性能を上げるための添加剤を添加することを考えると、水性分散液中のマイクロカプセル化顔料の含有量が10重量部より少ない場合、添加剤の添

加量が制限される傾向にあるので、好ましくない。

【0090】本発明のアニオン性マイクロカプセル化顔料を含有する水性分散液を含有する記録液は、上記で説明したアニオン性マイクロカプセル化顔料含有水性分散液、水溶性有機溶剤、水等を混合して調製される。更に必要に応じて、水溶性樹脂、有機アミン、界面活性剤、防腐剤、粘度調整剤、pH調整剤、キレート化剤等を添加することもできる。

【0091】本発明の記録液中のアニオン性マイクロカプセル化顔料含有水性分散液の含有割合は、記録液としての色濃度や精細度、透明性、色相の彩度等を考慮すると、1～100重量%の範囲が好ましく、5～100重量%の範囲が特に好ましい。特に、記録液を直接提供することを考えれば、100重量%が好ましいことは言うまでもない。

【0092】記録液に用いる水溶性有機溶剤としては、例えば、メチルアルコール、エチルアルコール、n-ブチルアルコール、イソブチルアルコール、tert-ブチルアルコール、n-プロピルアルコール、イソプロピルアルコール等のアルコール類；ジメチルホルムアルデヒド、ジメチルアセトアミド等のアミド類；アセトン、メチルエチルケトン等のケトン類；テトラヒドロフラン、ジオキサン、エチレングリコールメチルエーテル、エチレングリコールエチルエーテル、ジエチレングリコールメチルエーテル、ジエチレングリコールエチルエーテル、トリエチレングリコールモノメチルエーテル、トリエチレンエチレングリコールモノエチルエーテル等のエーテル類；エチレングリコール、プロピレングリコール、ブチレングリコール、トリエチレングリコール、1,2,6-ヘキサントリオール、チオジグリコール、ジエチレングリコール、ポリエチレングリコール、ポリプロピレングリコール、グリセリン等の多価アルコール類；N-メチルピロリドン、1,3-ジメチル-2-イミダゾリジノン等が挙げられる。これらの水溶性有機溶剤の中でも、多価アルコール類とエーテル類が好ましい。

【0093】記録液中の水溶性有機溶剤の含有割合は、95重量%以下が好ましく、0～80重量%の範囲が特に好ましい。

【0094】記録液に必要なに応じて用いる水溶性樹脂としては、例えば、にかわ、ゼラチン、カゼイン、アルブミン、アラビアゴム、フィッシュグリュースなどの天然タンパク質やアルギン酸、メチルセルロース、カルボキシメチルセルロース、ポリエチレンオキシド、ヒドロキシエチルセルロース、ポリビニルアルコール、ポリアクリルアミド、芳香族アミド、ポリアクリル酸、ポリビニルエーテル、ポリビニルピロリドン、アクリル、ポリエステル等の合成高分子等が挙げられる。

【0095】水溶性樹脂は、定着性や粘度調節、速乾性を挙げる目的で、必要に応じて使用されるものであり、



記録液に使用する場合の記録液中の水溶性樹脂の含有割合は、30重量%以下が好ましく、20重量%以下が特に好ましい。

【0096】記録液に必要なに応じて用いる有機アミンとしては、例えば、エタノールアミン、ジエタノールアミン、トリエタノールアミン、N-メチルエタノールアミン、N-エチルジエタノールアミン、2-アミノ-2-メチルプロパノール、2-エチル-2-アミノ-1, 3-プロパンジオール、2-(アミノエチル)エタノールアミン、トリス(ヒドロキシメチル)アミノメタン、アンモニア、ピペリジン、モルフォリン等が挙げられる。

【0097】本発明の記録液の製造方法は、何等顔料を分散するような分散機を必要とせずディスパー等の簡単な攪拌機で、アニオン性マイクロカプセル化顔料含有水性分散液、水溶性有機溶剤、水、水溶性樹脂等を攪拌混合する操作のみでも製造することができる。また、必要に応じて、界面活性剤、防腐剤、粘度調整剤、pH調整剤、キレート化剤等を攪拌時に添加して製造する。

【0098】このようにして製造された記録液は、ジェットプリンター等の画像記録用いることにより、記録画像の精細度、発色性、透明性、耐水性や再分散性に優れ、分散工程の省力化により記録液の製造コストの大幅な低減が図れる。

【0099】

【実施例】以下、実施例及び比較例を用いて、本発明を更に詳細に説明する。以下において、「部」及び「%」は、特に断りがない限り、『重量部』及び『重量%』を表わす。

【0100】<合成例1>(アニオン性基含有有機高分子化合物類の合成)

n-ブチルメタクリレート175部、n-ブチルアクリレート10.7部、β-ヒドロキシエチルメタクリレート37.5部、メタクリル酸26.8部及び「パーブチル O」(日本油脂(株)製のtert-ブチルパーオキシオクトエート)5.0部から成る混合液を調製した。

【0101】次に、メチルエチルケトン250部をフラスコに仕込んだ後、窒素シール下に、攪拌しながら、75℃まで昇温させた後、上記の混合液を2時間に亘って滴下し、更に同温度で15時間反応させて、固形分の酸価が70、数平均分子量12500のビニル系樹脂の溶液を得た。この樹脂溶液の不揮発分は48%であった。以下、これを樹脂溶液(A-1)と略記する。

【0102】<合成例2>(アニオン性基含有有機高分子化合物類の合成)

スチレン43部、n-ブチルアクリレート87.5部、β-ヒドロキシエチルメタクリレート37.5部、メタクリル酸19.5部及び「パーブチル O」5.0部から成る混合液を調製した。

【0103】次に、メチルエチルケトン250部をフラスコに仕込んだ後、窒素シール下に、攪拌しながら、7

5℃まで昇温させた後、上記の混合液を2時間に亘って滴下し、更に同温度で15時間反応させて、固形分の酸価が48、数平均分子量14000のビニル系樹脂の溶液を得た。この樹脂溶液の不揮発分は49%であった。

以下、これを樹脂溶液(A-2)と略記する。

【0104】<合成例3>(アニオン性基含有有機高分子化合物類の合成)

スチレン100部、n-ブチルアクリレート40.3部、β-ヒドロキシエチルメタクリレート37.5部、メタクリル酸9.7部及び「パーブチル O」5.0部から成る混合液を調製した。

【0105】次に、メチルエチルケトン250部をフラスコに仕込んだ後、窒素シール下に、攪拌しながら、75℃まで昇温させた後、上記の混合液を2時間に亘って滴下し、更に同温度で15時間反応させて、固形分の酸価が24、数平均分子量15000のビニル系樹脂の溶液を得た。この樹脂溶液の不揮発分は49%であった。以下、これを樹脂溶液(A-3)と略記する。

【0106】<合成例4>(アニオン性基含有有機高分子化合物類の合成)

n-ブチルメタクリレート175部、n-ブチルアクリレート10.7部、β-ヒドロキシエチルメタクリレート37.5部、メタクリル酸26.8部及び「パーブチル O」20.0部から成る混合液を調製した。

【0107】次に、メチルエチルケトン250部をフラスコに仕込んだ後、窒素シール下に、攪拌しながら、75℃まで昇温させた後、上記の混合液を2時間に亘って滴下し、更に同温度で15時間反応させて、固形分の酸価が68、数平均分子量5600のビニル系樹脂の溶液を得た。この樹脂溶液の不揮発分は50%であった。以下、これを樹脂溶液(A-4)と略記する。

【0108】<合成例5>(アニオン性基含有有機高分子化合物類の合成)

n-ブチルメタクリレート153.8部、n-ブチルアクリレート20.4部、β-ヒドロキシエチルメタクリレート37.5部、メタクリル酸38.3部及び「パーブチル O」5.0部から成る混合液を調製した。次に、メチルエチルケトン250部をフラスコに仕込んだ後、窒素シール下に

【0109】、攪拌しながら、75℃まで昇温させた後、上記の混合液を2時間に亘って滴下し、更に同温度で15時間反応させて、固形分の酸価が98、数平均分子量12500のビニル系樹脂の溶液を得た。この樹脂溶液の不揮発分は51%であった。以下、これを樹脂溶液(A-5)と略記する。

【0110】<合成例6>(アニオン性基含有有機高分子化合物類の合成)

n-ブチルメタクリレート171.4部、n-ブチルアクリレート6.3部、β-ヒドロキシエチルメタクリレート37.5部、アクリル酸34.8部及び「パーブチ

ル 0」20.0部から成る混合液を調製した。

【0111】次に、メチルエチルケトン250部をフラスコに仕込んだ後、窒素シール下に攪拌しながら75℃まで昇温させた後、上記の混合液を2時間に亘って滴下し、更に同温度で15時間反応させて、固形分の酸価が95、数平均分子量8800のビニル系樹脂の溶液を得た。この樹脂溶液の不揮発分は50%であった。以下、これを樹脂溶液(A-6)と略記する。

【0112】<合成例7>(アニオン性基含有有機高分子化合物類の合成—ゲル化処理用)

n-ブチルメタクリレート83.8部、n-ブチルアクリレート89.4部、β-ヒドロキシエチルメタクリレ

ート37.5部、メタクリル酸26.7部、グリシジルメタクリレート12.5部及び「パーブチル 0」20.0部から成る混合液を調製した。

【0113】次に、メチルエチルケトン250部をフラスコに仕込んだ後、窒素シール下に、攪拌しながら、75℃まで昇温させた後、上記の混合液を2時間に亘って滴下し、更に同温度で15時間反応させて、固形分の酸価が69、数平均分子量10400のビニル系樹脂の溶液を得た。この樹脂溶液の不揮発分は50%であった。以下、これを樹脂溶液(A-7)と略記する。

【0114】

【表1】

	樹脂溶液	分子量	酸価	不揮発分%
合成例1	A-1	12500	70	48
合成例2	A-2	14000	48	49
合成例3	A-3	15000	24	49
合成例4	A-4	5600	68	50
合成例5	A-5	12500	98	51
合成例6	A-6	8800	95	50
合成例7	A-7	10400	69	50

【0115】<製造例1>(銅フタロシアニンブルーのアニオン性マイクロカプセル化顔料含有水性分散液の製造)

合成例5で得た樹脂溶液(A-5)22.1部、「ファストゲン・ブルー・TGR」(大日本インキ化学工業(株)製のC.I.ピグメント・ブルー15、平均粒子径50nm、最大粒子径100nm)14.25部、分散助剤としてジメチルアミノメチル銅フタロシアニン0.75部、メチルエチルケトン78.2部、「スーパー・ベッカミン L-109-60」(大日本インキ化学工業(株)製のメラミン樹脂)4.7部及びセラミック・ビーズ300部を、ステンレス製容器に入れた後、その混合物を、ビーズミル分散機を用いて分散させて、マイクロカプセル化顔料用ペーストを調製した。

【0116】次に、上記マイクロカプセル化顔料用ペースト40.0部及びジメチルアミノエタノール0.4部をポリカップに入れた後、攪拌機を用いて混合し、有機相とした後、この有機相を攪拌しながら、かつ有機相に45KHzの超音波を照射しながら、有機相中にイオン交換水50部を12分間かけて滴下して、自己分散(転相乳化)を行ない、アニオン性マイクロカプセル化顔料

含有水性分散液を得た。

【0117】更に、このマイクロカプセル化顔料含有水性分散液を、85℃で蒸留することによって溶剤を留去させた後、同温度で5時間保持して、カプセル壁のゲル化処理を行なった。

【0118】このようにして得たアニオン性マイクロカプセル化顔料含有水性分散液(MC-1)中のマイクロカプセル化顔料の粒径を「UPA-150」(日機装社製のレーザードップラー方式粒度分布測定機)を用いて測定した結果、マイクロカプセル化顔料の体積平均粒子径は148nmで、最大粒子径は1000nm以上の粒子は0%であった。また、マイクロカプセル化顔料含有水性分散液の不揮発分濃度は24.5%で、マイクロカプセル中の顔料の含有量は51.7%であった。

【0119】<製造例2>(銅フタロシアニンブルーのアニオン性マイクロカプセル化顔料含有水性分散液の製造)

(1) 顔料混練工程

容量250mlのガラスビンに、合成例4で得た樹脂溶液(A-4)15.0部、ジメチルエタノールアミン0.8部及び「ファストゲン・ブルー・TGR」15部

を加え、イオン交換水を加えて総量が75部となるようにした後、平均粒子径が0.5mmのジルコニアビーズ250gを加えた後、ペイントシェーカーを用いて4時間混練を行なった。混練終了後、ガラスビーズを濾別して、塩基で中和されたカルボキシル基を有する樹脂と顔料から成る分散体を水に分散したものを得た。

#### 【0120】(2) 酸析

塩基で中和されたカルボキシル基を有する樹脂と顔料から成る分散体を水に分散したものに、水を加えて倍に希釈した後、ディスペーで攪拌しながら、1規定塩酸を樹脂が不溶化して顔料に固着するまで加えた。この時のpHは3~5であった。

#### 【0121】(3) 濾過及び水洗

樹脂が固着した顔料を含有する水性媒体を吸引濾過した後、塩を水洗して、含水ケーキを得た。

【0122】(4) 中和、及び、水性媒体への再分散  
含水ケーキをディスペーを用いて攪拌しながら、分散体のpHが8.5~9.5となるまでジメチルエタノールアミンの10%水溶液を加えた。更に、1時間攪拌を続けた後、水を加えて、不揮発分が20%となるように調整して、アニオン性マイクロカプセル化顔料含有水性分散液(MC-2)を得た。

【0123】製造例1と同様にしてアニオン性マイクロカプセル化顔料含有水性分散液(MC-2)中のマイクロカプセル化顔料の粒径を測定した結果、マイクロカプセル化顔料の体積平均粒子径は170nmで、1000nm以上の粒子は0%であった。また、マイクロカプセル中の顔料の含有量は67%であった。

【0124】<製造例3>(無機塩による銅フタロシアニンブルーのアニオン性マイクロカプセル化顔料含有水性分散液の製造)

#### (1) 顔料混練工程

製造例2と同様にして、塩基で中和されたカルボキシル基を有する樹脂と顔料から成る分散体を水に分散したものを得た。

#### 【0125】(2) 酸析

塩基で中和されたカルボキシル基を有する樹脂と顔料から成る分散体を水に分散したものに、水を加えて倍に希釈した後、ディスペーで攪拌しながら、1規定塩酸を樹脂が不溶化して顔料に固着するまで加えた。この時のpHは3~5であった。

#### 【0126】(3) 濾過及び水洗

樹脂が固着した顔料を含有する水性媒体を吸引濾過した後、塩を水洗して、含水ケーキを得た。

【0127】(4) 中和、及び、水性媒体への再分散  
含水ケーキをディスペーを用いて攪拌しながら、分散体のpHが8.5~9.5となるまで10%水酸化ナトリウム水溶液を加えた。更に、1時間攪拌を続けた後、水を加えて、不揮発分が20%となるように調整して、アニオン性マイクロカプセル化顔料含有水性分散液(MC

-3)を得た。

【0128】製造例1と同様にしてアニオン性マイクロカプセル化顔料含有水性分散液(MC-3)中のマイクロカプセル化顔料の粒径を測定した結果、マイクロカプセル化顔料の体積平均粒子径は182nmで、1000nm以上の粒子は0%であった。また、マイクロカプセル中の顔料の含有量は67%であった。

【0129】<製造例4>(銅フタロシアニンブルーのアニオン性マイクロカプセル化顔料含有水性分散液の製造)

合成例2で得た樹脂溶液(A-2)中のカルボキシル基を有する樹脂を、ジメチルエタノールアミンを用いて100%中和したものを使用した以外は製造例2と同様にして、顔料混練、酸析、濾過及び水洗、中和及び再分散を行ない、不揮発分が20%のアニオン性マイクロカプセル化顔料含有水性分散液(MC-4)を得た。

【0130】製造例2と同様にしてアニオン性マイクロカプセル化顔料含有水性分散液(MC-4)中のマイクロカプセル化顔料の粒径を測定した結果、マイクロカプセル化顔料の体積平均粒子径は218nmで、1000nm以上の粒子は0%であった。また、マイクロカプセル中の顔料の含有量は67%であった。

【0131】<製造例5>(酸価25のアニオン性有機高分子化合物類を使用した銅フタロシアニンブルーのアニオン性マイクロカプセル化顔料含有水性分散液の製造)

#### (1) 顔料混練工程

合成例3で得た樹脂溶液(A-3)中のカルボキシル基を有する樹脂を、ジメチルエタノールアミンを用いて100%中和した。容量250mlのガラスビンに、中和した樹脂を固形分換算で7.5部及び「ファストゲン・ブルー・TGR」15部を加え、樹脂が溶解する量のメチルエチルケトンを加え、イオン交換水を加えて総量が75部となるようにした後、平均粒子径が0.5mmのジルコニアビーズ250gを加え、ペイントシェーカーを用いて4時間混練を行なった。混練終了後、ガラスビーズを濾別して、塩基で中和されたカルボキシル基を有する樹脂と顔料から成る分散体を水に分散したものを得た。

#### 【0132】(2) 酸析

塩基で中和されたカルボキシル基を有する樹脂と顔料から成る分散体を水に分散したものに水を加えて倍に希釈した後、ディスペーで攪拌しながら、1規定塩酸を樹脂が不溶化して顔料に固着するまで加えた。この時のpHは3~5であった。

#### 【0133】(3) 濾過及び水洗

樹脂が固着した顔料を含有する水性媒体を吸引濾過した後、塩を水洗して、含水ケーキを得た。

【0134】(4) 中和、及び、水性媒体への再分散  
含水ケーキをディスペーを用いて攪拌しながら、分散体

のpHが8.5~9.5となるまでジメチルエタノールアミンの10%水溶液を加えた。更に、1時間攪拌を続けた後、水を加えて、不揮発分が20%となるように調整して、アニオン性マイクロカプセル化顔料含有水性分散液(MC-5)を得た。

【0135】製造例1と同様にしてアニオン性マイクロカプセル化顔料含有水性分散液(MC-5)中のマイクロカプセル化顔料の粒径を測定した結果、マイクロカプセル化顔料の体積平均粒子径は650nmで、1000nm以上の粒子は17%であった。また、マイクロカプセル中の顔料の含有量は67%であった。

【0136】<製造例6>(マゼンタ色のアニオン性マイクロカプセル化顔料含有水性分散液の製造)  
合成例1で得た樹脂溶液(A-1)23.4部、「ファストゲン・スーパー・マゼンタ・RTS」(大日本インキ化学工業(株)製のC. I. ピグメント・レッド122、平均粒子径45nm、最大粒子径100nm)14.25部、分散助剤としてジメチルアミノメチルキナクリドン0.75部、メチルエチルケトン76.9部、「スーパー・ベッカミン L-109-60」(大日本インキ化学工業(株)製のメラミン樹脂)4.7部及びセラミック・ビーズ300部を、ステンレス製容器に入れた後、その混合物を、ビーズミル分散機を用いて分散させて、マイクロカプセル化顔料用ペーストを調製した。

【0137】次に、上記マイクロカプセル化顔料用ペースト40.0部及びジメチルアミノエタノール0.4部をポリカップに入れた後、攪拌機を用いて混合して、有機相とした後、この有機相を攪拌しながら、かつ有機相に45KHzの超音波を照射しながら、有機相中にイオン交換水50部を12分間かけて滴下して、自己分散(転相乳化)を行ない、アニオン性マイクロカプセル化顔料含有水性分散液を得た。

【0138】更に、このマイクロカプセル化顔料含有水性分散液を、85℃で蒸留することによって溶剤を留去させた後、同温度で5時間保持して、カプセル壁のゲル化処理を行なった。

【0139】このようにして得たアニオン性マイクロカプセル化顔料含有水性分散液(MC-6)中のマイクロカプセル化顔料の粒径を、製造例1と同様にして測定した結果、マイクロカプセル化顔料の体積平均粒子径は145nmで、最大粒子径は1000nm以上の粒子は0%であった。また、マイクロカプセル化顔料含有水性分散液の不揮発分濃度は23.2%で、マイクロカプセル中の顔料の含有量は51.7%であった。

【0140】<製造例7>(マゼンタ色のアニオン性マイクロカプセル化顔料含有水性分散液の製造)

#### (1) 顔料混練工程

容量250mlのガラスビンに、合成例4で得た樹脂溶液(A-4)15.0部、ジメチルエタノールアミン0.8部及び「ファストゲン・スーパー・マゼンタ・R

TS」(大日本インキ化学工業(株)製のC. I. ピグメント・レッド122、平均粒子径45nm、最大粒子径100nm)15部を加え、イオン交換水を加えて総量が75部となるようにした後、平均粒子径が0.5mmのジルコニアビーズ250gを加えた後、ペイントシェーカーにより4時間混練を行なった。混練終了後、ガラスビーズを濾別して、塩基で中和されたカルボキシル基を有する樹脂と顔料から成る分散体を水に分散したものを得た。

#### 【0141】(2) 酸析

塩基で中和されたカルボキシル基を有する樹脂と顔料から成る分散体を水に分散したものに水を加えて倍に希釈した後、ディスパーで攪拌しながら、1規定塩酸を樹脂が不溶化して顔料に固着するまで加えた。この時のpHは3~5であった。

#### 【0142】(3) 濾過及び水洗

樹脂が固着した顔料を含有する水性媒体を吸引濾過した後、塩を水洗して、含水ケーキを得た。

【0143】(4) 中和、及び、水性媒体への再分散  
含水ケーキをディスパーを用いて攪拌しながら、分散体のpHが8.5~9.5となるまでジメチルエタノールアミンの10%水溶液を加えた。更に、1時間攪拌を続けた後、水を加えて、不揮発分が20%となるように調整して、アニオン性マイクロカプセル化顔料含有水性分散液(MC-7)を得た。

【0144】製造例1と同様にして、アニオン性マイクロカプセル化顔料含有水性分散液(MC-7)中のマイクロカプセル化顔料の粒径を測定した結果、マイクロカプセル化顔料の体積平均粒子径は176nmで、1000nm以上の粒子は0%であった。また、マイクロカプセル中の顔料の含有量は67%であった。

【0145】<製造例8>(有機顔料の含有量が83%のマゼンタ色のアニオン性マイクロカプセル化顔料含有水性分散液の製造)

製造例7において、顔料混練工程で使用する樹脂溶液(A-4)の使用量を6.0部とした以外は、製造例7と同様にして顔料混練、酸析、濾過及び水洗、中和及び再分散を行ない、不揮発分が20%のアニオン性マイクロカプセル化顔料含有水性分散液(MC-8)を得た。

【0146】製造例1と同様にしてアニオン性マイクロカプセル化顔料含有水性分散液(MC-8)中のマイクロカプセル化顔料の粒径を測定した結果、マイクロカプセル化顔料の体積平均粒子径は250nmで、1000nm以上の粒子は0%であった。また、マイクロカプセル中の顔料の含有量は83%であった。

【0147】<製造例9>(有機顔料の含有量が75%のマゼンタ色のアニオン性マイクロカプセル化顔料含有水性分散液の製造)

製造例7において、顔料混練工程で使用する樹脂溶液(A-4)の使用量を10.0部とし、樹脂溶液(A-

4)と共にエチルエチルケトン5.0部を使用した以外は、製造例7と同様にして、顔料混練、酸析、濾過及び水洗、中和及び再分散を行ない、不揮発分が20%のアニオン性マイクロカプセル化顔料含有水性分散液(MC-9)を得た。

【0148】製造例1と同様にしてアニオン性マイクロカプセル化顔料含有水性分散液(MC-9)中のマイクロカプセル化顔料の粒径を測定した結果、マイクロカプセル化顔料の体積平均粒子径は180nmで、1000nm以上の粒子は0%であった。また、マイクロカプセル中の顔料の含有量は75%であった。

【0149】<製造例10>(有機顔料の含有量が33%のマゼンタ色のアニオン性マイクロカプセル化顔料含有水性分散液の製造)

#### (1) 顔料分散工程

容量250mlのガラスビンに、合成例4で得た樹脂溶液(A-4)20.0部、ジメチルエタノールアミン1.1部及び「ファストゲン・スーパー・マゼンタ・RTS」5.0部を加え、イオン交換水を加えて総量が75部となるようにした後、平均粒子径が0.5mmのジルコニアビーズ250gを加えた後、ペイントシェーカーを用いて4時間混練を行なった。混練終了後、ガラスビーズを濾別して、塩基で中和されたカルボキシル基を有する樹脂と顔料から成る分散体を水に分散したものを得た。

【0150】次に、製造例7と同様にして、酸析、濾過及び水洗、中和及び再分散を行ない、不揮発分が20%のアニオン性マイクロカプセル化顔料含有水性分散液(MC-10)を得た。

【0151】製造例1と同様にして、アニオン性マイクロカプセル化顔料含有水性分散液(MC-10)中のマイクロカプセル化顔料の粒径を測定した結果、マイクロカプセル化顔料の体積平均粒子径は224nmで、1000nm以上の粒子は0%であった。また、マイクロカプセル中の顔料の含有量は33%であった。

【0152】<製造例11>(平均粒子径が250nmの有機顔料を使用したマゼンタ色のアニオン性マイクロカプセル化顔料含有水性分散液の製造)

製造例7において、「ファストゲン・スーパー・マゼンタ・RTS」に代えて、「クロモフタル・レッド・DPP-BO」(チバ・ガイギー社製のC. I. ピグメント・レッド254、平均粒子径250nm、最大粒子径400nm)を用いた以外は、製造例7と同様にして、顔料混練、酸析、濾過及び水洗、中和及び再分散を行ない、不揮発分が20%のアニオン性マイクロカプセル化顔料含有水性分散液(MC-11)を得た。

【0153】製造例1と同様にして、アニオン性マイクロカプセル化顔料含有水性分散液(MC-11)中のマイクロカプセル化顔料の粒径を測定した結果、マイクロカプセル化顔料の体積平均粒子径は283nmで、最大

粒子径は1000nm以上の粒子は0%であった。また、マイクロカプセル中の顔料の含有量は67%であった。

【0154】<製造例12>(イエロー色のアニオン性マイクロカプセル化顔料含有水性分散液の製造)

合成例1で得た樹脂溶液(A-1)23.4部、「シムラーファスト・イエロー・8GTF」(大日本インキ化学工業(株)製のC. I. ピグメント・イエロー17、平均粒子径60nm、最大粒子径120nm)15.0部、メチルエチルケトン76.9部、「スーパー・ベッカミン L-109-60」(大日本インキ化学工業(株)製のメラミン樹脂)4.7部及びセラミック・ビーズ300部を、ステンレス製容器に入れた後、その混合物を、ビーズミル分散機を用いて分散させて、マイクロカプセル化顔料用ペーストを調製した。

【0155】次に、上記マイクロカプセル化顔料用ペースト40.0部及びジメチルアミノエタノール0.4部をポリカップに入れた後、攪拌機を用いて混合して、有機相とした後、この有機相を攪拌しながら、かつ有機相に45KHzの超音波を照射しながら、有機相中にイオン交換水50部を12分間かけて滴下して、自己分散(転相乳化)を行ない、アニオン性マイクロカプセル化顔料含有水性分散液を得た。

【0156】更に、このマイクロカプセル化顔料含有水性分散液を、85℃で蒸留することによって溶剤を留去させた後、同温度で5時間保持して、カプセル壁のゲル化処理を行なった。

【0157】このようにして得たアニオン性マイクロカプセル化顔料含有水性分散液(MC-12)中のマイクロカプセル化顔料の粒径を、製造例1と同様にして測定した結果、マイクロカプセル化顔料の体積平均粒子径は191nmで、最大粒子径は1000nm以上の粒子は0%であった。また、マイクロカプセル化顔料含有水性分散液の不揮発分濃度は23.8%で、マイクロカプセル中の顔料の含有量は51.7%であった。

【0158】<製造例13>(イエロー色のアニオン性マイクロカプセル化顔料含有水性分散液の製造)

#### (1) 顔料混練工程

容量250mlのガラスビンに、合成例1で得た樹脂溶液(A-1)15.6部、ジメチルエタノールアミン0.8部及び「シムラーファスト・イエロー・8GTF」15部を加え、イオン交換水を加えて総量が75部となるようにした後、平均粒子径が0.5mmのジルコニアビーズ250gを加えた後、ペイントシェーカーを用いて4時間混練を行なった。混練終了後、ガラスビーズを濾別して、塩基で中和されたカルボキシル基を有する樹脂と顔料から成る分散体を水に分散したものを得た。

#### 【0159】(2) 酸析

塩基で中和されたカルボキシル基を有する樹脂と顔料が

ら成る分散体を水に分散したものに水を加えて倍に希釈した後、ディスパーで攪拌しながら、1規定塩酸を樹脂が不溶化して顔料に固着するまで加えた。この時のpHは3～5であった。

#### 【0160】(3) 濾過及び水洗

樹脂が固着した顔料を含有する水性媒体を吸引濾過した後、塩を水洗して、含水ケーキを得た。

【0161】(4) 中和、及び、水性媒体への再分散  
含水ケーキをディスパーを用いて攪拌しながら、分散体のpHが8.5～9.5となるまでジメチルエタノールアミンの10%水溶液を加えた。更に、1時間攪拌を続けた後、水を加えて、不揮発分が20%となるように調整して、イエロー色のアニオン性マイクロカプセル化顔料含有水性分散液(MC-13)を得た。

【0162】製造例1と同様にして、アニオン性マイクロカプセル化顔料含有水性分散液(MC-13)中のマイクロカプセル化顔料の粒径を測定した結果、マイクロカプセル化顔料の体積平均粒子径は183nmで、1000nm以上の粒子は0%であった。また、マイクロカプセル中の顔料の含有量は67%であった。

【0163】<製造例14>(平均粒子径が220nmの有機顔料を使用したイエロー色のアニオン性マイクロカプセル化顔料含有水性分散液の製造)

製造例13において、「シムラーファスト・イエロー・8GTF」に代えて、「シムラーファスト・イエロー・4192」(大日本インキ化学工業(株)製のC. I. ピグメント・イエロー154、平均粒子径220nm、最大粒子径350nm)を用いた以外は、製造例13と同様にして、顔料混練、酸析、濾過及び水洗、中和及び再分散を行ない、不揮発分が20%のアニオン性マイクロカプセル化顔料含有水性分散液(MC-14)を得た。

【0164】製造例1と同様にして、アニオン性マイクロカプセル化顔料含有水性分散液(MC-14)中のマイクロカプセル化顔料の粒径を測定した結果、マイクロカプセル化顔料の体積平均粒子径は245nmで、1000nm以上の粒子は0%であった。また、マイクロカプセル中の顔料の含有量は67%であった。

【0165】<製造例15>(不揮発性の塩基を使用したシアン色のアニオン性マイクロカプセル化顔料含有水性分散液の製造)

#### (1) 顔料混練工程

容量250mlのガラスビンに、合成例6で得た樹脂溶液(A-6)15.0部、ジメチルエタノールアミン1.1部及び「ファストゲン・ブルー・TGR」15部を加え、イオン交換水を加えて総量が75部となるようにした後、平均粒子径が0.5mmのジルコニアビーズ250gを加えた後、ペイントシェーカーを用いて4時間混練を行なった。混練終了後、ガラスビーズを濾別して、塩基で中和されたカルボキシル基を有する樹脂と顔料から成る分散体を水に分散したものを得た。

#### 【0166】(2) 酸析

塩基で中和されたカルボキシル基を有する樹脂と顔料から成る分散体を水に分散したものに水を加えて倍に希釈した後、ディスパーで攪拌しながら、1規定塩酸を樹脂が不溶化して顔料に固着するまで加えた。この時のpHは3～5であった。

#### 【0167】(3) 濾過及び水洗

樹脂が固着した顔料を含有する水性媒体を吸引濾過した後、塩を水洗して、含水ケーキを得た。

【0168】(4) 中和、及び、水性媒体への再分散  
含水ケーキをディスパーを用いて攪拌しながら、分散体のpHが8.5～9.5となるまで10%水酸化ナトリウム水溶液を加えた。更に、1時間攪拌を続けた後、水を加えて、不揮発分が20%となるように調整して、ブルー色のアニオン性マイクロカプセル化顔料含有水性分散液(MC-15)を得た。

【0169】製造例1と同様にして、アニオン性マイクロカプセル化顔料含有水性分散液(MC-15)中のマイクロカプセル化顔料の粒径を測定した結果、マイクロカプセル化顔料の体積平均粒子径は152nmで、1000nm以上の粒子は0%であった。また、マイクロカプセル中の顔料の含有量は67%であった。

【0170】<製造例16>(不揮発性の塩基を使用したマゼンタ色のアニオン性マイクロカプセル化顔料含有水性分散液の製造)

製造例15において、「ファストゲン・ブルー・TGR」に代えて、「ファストゲン・スーパー・マゼンタ・RTS」を用い、更に中和用の10%水酸化ナトリウム水溶液に代えて10%水酸化カリウム水溶液を用いた以外は、製造例15と同様にして、顔料混練、酸析、濾過及び水洗、中和及び再分散を行ない、不揮発分が20%のアニオン性マイクロカプセル化顔料含有水性分散液(MC-16)を得た。

【0171】製造例1と同様にして、アニオン性マイクロカプセル化顔料含有水性分散液(MC-16)中のマイクロカプセル化顔料の粒径を測定した結果、マイクロカプセル化顔料の体積平均粒子径は、178nmで、1000nm以上の粒子は0%であった。また、マイクロカプセル中の顔料の含有量は67%であった。

【0172】<製造例17>(不揮発性の塩基を使用したイエロー色のアニオン性マイクロカプセル化顔料含有水性分散液の製造)

製造例15において、「ファストゲン・ブルー・TGR」に代えて、「シムラーファスト・イエロー・8GTF」を用い、更に中和用の10%水酸化ナトリウム水溶液に代えて10%水酸化リチウム水溶液を用いた以外は、製造例15と同様にして、顔料混練、酸析、濾過及び水洗、中和及び再分散を行ない、不揮発分が20%のアニオン性マイクロカプセル化顔料含有水性分散液(MC-17)を得た。



【0173】製造例1と同様にして、アニオン性マイクロカプセル化顔料含有水性分散液（MC-17）中のマイクロカプセル化顔料の粒径を測定した結果、マイクロカプセル化顔料の体積平均粒子径は182nmで、1000nm以上の粒子は0%であった。また、マイクロカプセル中の顔料の含有量は67%であった。

【0174】＜製造例18＞（カプセル壁のゲル化処理をしたカーボンブラックのアニオン性マイクロカプセル化顔料含有水性分散液の製造）

（1）顔料混練工程

容量250mlのガラスビンに、合成例7で得た樹脂溶液（A-7）15.0部、ジメチルエタノールアミン0.8部及び「MA-600（三菱化学社製の中級カーボンブラック：平均粒子径18nm）」15部を加え、イオン交換水を加えて総量が75部となるようにした後、平均粒子径が0.5mmのジルコニアビーズ250部を加えた後、ペイントシェーカーを用いて4時間混練を行なった。混練終了後、ガラスビーズを濾別して、塩基で中和されたカルボキシル基を有する樹脂と顔料から成る分散体を水に分散したものを得た。

【0175】（2）ゲル化処理

塩基で中和されたカルボキシル基を有する樹脂と顔料から成る分散体を水に分散したものに水を加えて3倍に希釈した後、オートクレーブ中で、120℃で加熱ゲル化

処理をした。

【0176】（3）酸析

ゲル化処理をした後、常温で、ディスパーで攪拌しながら、1規定塩酸を樹脂が不溶化して顔料に固着するまで加えた。この時のpHは3～5であった。

【0177】（4）濾過及び水洗

樹脂が固着した顔料を含有する水性媒体を吸引濾過した後、塩を水洗して、含水ケーキを得た。

【0178】（5）中和、及び、水性媒体への再分散  
含水ケーキをディスパーを用いて攪拌しながら、分散体のpHが8.5～9.5となるまで10%ジメチルアミノエタノール水溶液を加えた。更に、1時間攪拌を続けた後、水を加えて、不揮発分が20%となるように調整して、カーボンブラックのアニオン性マイクロカプセル化顔料含有水性分散液（MC-18）を得た。

【0179】製造例1と同様にして、アニオン性マイクロカプセル化顔料含有水性分散液（MC-18）中のマイクロカプセル化顔料の粒径を測定した結果、マイクロカプセル化顔料の体積平均粒子径は149nmで、1000nm以上の粒子は0%であった。また、マイクロカプセル中の顔料の含有量は67%であった。

【0180】

【表2】

	樹脂溶液	顔 料	方法	7ミソ	粒子径	N.V.	粗粒	顔料分
製造例1	A-5	TGR	転相	DMAE	148nm	24.5%	0%	51.7%
製造例2	A-4	TGR	酸析	DMAE	170nm	20%	0%	67%
製造例3	A-4	TGR	酸析	NaOH	182nm	20%	0%	67%
製造例4	A-2	TGR	酸析	DMAE	218nm	20%	0%	67%
製造例5	A-3	TGR	酸析	DMAE	650nm	20%	17%	67%
製造例6	A-1	RTS	転相	DMAE	145nm	23.2%	0%	51.7%
製造例7	A-4	RTS	酸析	DMAE	176nm	20%	0%	67%
製造例8	A-4	RTS	酸析	DMAE	250nm	20%	0%	83%
製造例9	A-4	RTS	酸析	DMAE	180nm	20%	0%	75%
製造例10	A-4	RTS	酸析	DMAE	224nm	20%	0%	33%

【0181】

【表3】

	樹脂溶液	顔 料	方法	7ミシ	粒子径	N. V	粗粒	顔料分
製造例11	A-4	DPP	酸析	DMAE	283nm	20%	0%	67%
製造例12	A-1	8GTF	転相	DMAE	191nm	23.8%	0%	51.7%
製造例13	A-1	8GTF	酸析	DMAE	183nm	20%	0%	67%
製造例14	A-1	4192	酸析	DMAE	245nm	20%	0%	67%
製造例15	A-6	TGR	酸析	NaOH	152nm	20%	0%	67%
製造例16	A-6	RTS	酸析	KOH	178nm	20%	0%	67%
製造例17	A-6	8GTF	酸析	LiOH	178nm	20%	0%	67%
製造例18	A-7	CB	酸析	DMAE	149nm	20%	0%	67%

【0182】表2及び表3における略号は、以下の通りである。

TGR : 「ファストゲン・ブルー・TGR」(大日本インキ化学工業(株)製のC. I. ピグメント・ブルー15)

RTS : 「ファストゲン・スーパー・マゼンタ・RTS」(大日本インキ化学工業(株)製のC. I. ピグメント・レッド122)

DPP : 「クロモフタル・レッド・DPP-BO」(チバ・ガイギー社製のC. I. ピグメント・レッド254)

8GTF : 「シムラーファスト・イエロー・8GTF」(大日本インキ化学工業(株)製のC. I. ピグメント・イエロー17)

4192 : 「シムラーファスト・イエロー・4192」(大日本インキ化学工業(株)製のC. I. ピグメント・イエロー154)

CB : カーボンブラック

DMAE : ジメチルアミノエタノール

粒子径 : マイクロカプセル化顔料の体積平均粒子径

N. V. : 不揮発分濃度

粗粒 : マイクロカプセル化顔料の粒径1000nm以上の粒子の割合

顔料分 : マイクロカプセル中の顔料の含有割合

【0183】<実施例1>(マイクロカプセル化顔料中の顔料含有量が67%のマイクロカプセル化顔料分散液を使用した記録液の製造)

製造例2で得たフタロシアニンブルーのアニオン性マイクロカプセル化顔料含有水性分散液(MC-2)37.5部に、エチレングリコール7.5部、グリセリン5.0部、ジエチレングリコールモノブチルエーテル0.5

部、エチレングリコールモノメチルエーテル15.0部、イソプロピルアルコール3.0部、ジエタノールアミン3.0部及びイオン交換水28.5部を混合して、顔料分が5.0%のシアン色の記録液を調製した。

【0184】<実施例2>(マイクロカプセル化顔料中の顔料含有量が67%のマイクロカプセル化顔料分散液を使用した記録液の製造)

実施例1において、製造例2で得たフタロシアニンブルーのアニオン性マイクロカプセル化顔料含有水性分散液(MC-2)に代えて、製造例7で得たマゼンタ色のアニオン性マイクロカプセル化顔料含有水性分散液(MC-7)を用いた以外は、実施例1と同様にして、マゼンタ色の記録液を調製した。

【0185】<実施例3>(マイクロカプセル化顔料中の顔料含有量が67%のマイクロカプセル化顔料分散液を使用した記録液の製造)

実施例1において、製造例2で得たフタロシアニンブルーのアニオン性マイクロカプセル化顔料含有水性分散液(MC-2)に代えて、製造例13で得たイエロー色のアニオン性マイクロカプセル化顔料含有水性分散液(MC-13)を用いた以外は、実施例1と同様にして、イエロー色の記録液を調製した。

【0186】実施例1、2及び3において、記録液を調製するに当たっては、特にビーズミルやロール等の分散機を必要とせず、単に混合するのみで調製できたので、分散設備が不要で、分散工程や労力を短縮でき、製造時間の短縮あるいは分散エネルギーの省力化ができ、生産性を大きく上げるとともに製造コストの削減することができた。また、これらに使用したアニオン性マイクロカプセル化顔料含有水性分散液は、アニオン性マイクロカプセル化顔料中の顔料分が67%と高く、また、水性分

散液中の顔料分も13.4%以上と高く、記録液としての性能を上げるために使用される水溶性樹脂や水溶性有機溶剤等の他の材料をかなりの量で添加可能であり、汎用性が高かった。

【0187】次に、これらシアン色、マゼンタ色及びイエロー色の記録液中のマイクロカプセル化顔料の体積平均粒子径及び30日間室温で貯蔵した後の体積平均粒子径及び粒子の沈降性を表4に示した。実施例1、2及び3で得た各記録液中のアニオン性マイクロカプセル化顔料の体積平均粒子径は、貯蔵前後でほぼ同等の値を示し、さらに粒子の沈降が見られず、従来のマイクロカプセル化顔料に比べ、貯蔵安定性及び分散安定性に非常に優れていることが明らかである。

【0188】次に、上記記録液を用いて、市販のバブルジェット方式のプリンターを用いて、シアン色、マゼンタ色及びイエロー色のカラー記録画像を、OHPシート及びコピー紙に記録した。この記録画像は、表6に示すように、精細度や色濃度が高く、演色性や透明性に優れていた。また、OHPシートに記録した画像は、透明性に優れているためにカラフルな投影図を示していた。OHPシート上の記録画像を水をつけて擦っても消えることがなく、耐水性にも優れていた。また、繰り返し使用しても、インクを吐出させるノズルが詰まることもなかった。

【0189】＜比較例1＞（マイクロカプセル化顔料の平均粒子径が650nmで最大粒子径が1000nmを越えるマイクロカプセル化顔料分散液を使用した記録液の製造）

実施例1において、製造例2で得たフタロシアニンブルーのアニオン性マイクロカプセル化顔料含有水性分散液（MC-2）に代えて、製造例5で得たフタロシアニンブルーのアニオン性マイクロカプセル化顔料含有水性分散液（MC-5）を使用した以外は、実施例1と同様にして、シアン色の記録液を調製した。

【0190】比較例1で得たシアン色の記録液中のマイクロカプセル化顔料の体積平均粒子径及び30日間室温で貯蔵した後の体積平均粒子径及び粒子の沈降性を表8に示した。本比較例の記録液中のアニオン性マイクロカプセル化顔料の体積平均粒子径は、貯蔵前後でほぼ同等の値を示したが、粒子の沈降が見られ、分散安定性が悪かった。

【0191】次に、上記記録液を用いて、市販のバブルジェットプリンターを用いて、シアン色のカラー記録画像を、OHPシート及びコピー紙に記録した。この記録画像は、表9に示すように、精細度や色濃度が低く、演色性や透明性に欠けていた。また、OHPシートに記録した画像は、不透明でカラフルな投影図を示さず、OHPシートには使用できなかった。また、繰り返し使用しているうちに、インクを吐出させるノズルが詰まり、プリンターの使用ができなくなった。

【0192】＜実施例4＞（マイクロカプセル化顔料中の顔料含有量が51.7%のマイクロカプセル化顔料分散液を使用した記録液の製造）

製造例1で得たフタロシアニンブルーのアニオン性マイクロカプセル化顔料含有水性分散液（MC-1）47.4部に、エチレングリコール20部、ジエタノールアミン3.0部及びイオン交換水29.6部を混合して、顔料分が6%のシアン色の記録液を調製した。

【0193】＜実施例5＞（マイクロカプセル化顔料中の顔料含有量が51.7%のマイクロカプセル化顔料分散液を使用した記録液の製造）

製造例6で得たマゼンタ色のアニオン性マイクロカプセル化顔料含有水性分散液（MC-6）50.0部に、エチレングリコール20部、ジエタノールアミン3.0部及びイオン交換水27.0部を混合して、顔料分が6%のマゼンタ色の記録液を調製した。

【0194】＜実施例6＞（マイクロカプセル化顔料中の顔料含有量が51.7%のマイクロカプセル化顔料分散液を使用した記録液の製造）

製造例12で得たイエロー色のアニオン性マイクロカプセル化顔料含有水性分散液（MC-12）48.8部に、エチレングリコール20部、ジエタノールアミン3.0部及びイオン交換水28.2部を混合して、顔料分が6%のイエロー色の記録液を調製した。

【0195】これら実施例4、5及び6において、記録液を調製するに当たっては、特にビーズミルやロール等の分散機を必要とせず、単に混合するのみで調製できたので、分散設備が不要で、分散工程や労力を短縮でき、製造時間の短縮あるいは分散エネルギーの省力化ができ、生産性を大きく上げるとともに製造コストの削減することができた。また、これらに使用したアニオン性マイクロカプセル化顔料含有水性分散液は、アニオン性マイクロカプセル化顔料中の顔料分が51.7%と高く、また、水性分散液中の顔料分も10%以上と高く、記録液としての性能を上げるために使用される水溶性有機溶剤等の他の材料をかなりの量で添加可能であり、汎用性が高かった。

【0196】これらシアン色、マゼンタ色及びイエロー色の記録液中のマイクロカプセル化顔料の体積平均粒子径及び30日間室温で貯蔵した後の体積平均粒子径及び粒子の沈降性を表4に示した。本実施例の記録液中のアニオン性マイクロカプセル化顔料の体積平均粒子径は、貯蔵前後でほぼ同等の値を示し、さらに粒子の沈降が見られず、従来のマイクロカプセル化顔料に比べ、貯蔵安定性及び分散安定性に非常に優れていることが明らかである。

【0197】次に、上記記録液を用いて、市販のピエゾ方式のインクジェットプリンターを用いて、シアン色、マゼンタ色及びイエロー色のカラー記録画像を、OHPシート及びコピー紙に記録した。この記録画像は、表6

に示すように、精細度や色濃度が高く、演色性や透明性に優れていた。また、OHPシートに記録した画像は、透明性に優れているためにカラフルな投影図を示していた。OHPシート上の記録画像を水をつけて擦っても消えることがなく、耐水性にも優れていた。また、繰り返し使用しても、インクを吐出させるノズルが詰まることもなかった。

【0198】＜実施例7＞（マイクロカプセル化顔料中の顔料含有量が67%のマイクロカプセル化顔料分散液を使用した記録液の製造）

製造例2で得たフタロシアニンブルーのアニオン性マイクロカプセル化顔料含有水性分散液（MC-2）44.8部に、酸価163、分子量25,000の不揮発分50%のスチレンアクリル酸樹脂のアンモニア水溶液5.0部（樹脂固形分2.5部に相当）、エチレングリコール20部、ジエタノールアミン3.0部及びイオン交換水27.2部を混合して、顔料分が6%のシアン色の記録液を調製した。

【0199】＜実施例8＞（マイクロカプセル化顔料中の顔料含有量が67%のマイクロカプセル化顔料分散液を使用した記録液の製造）

実施例7において、製造例2で得たフタロシアニンブルーのアニオン性マイクロカプセル化顔料含有水性分散液（MC-2）に代えて、製造例7で得たマゼンタ色のアニオン性マイクロカプセル化顔料含有水性分散液（MC-7）を使用した以外は、実施例7と同様にして、マゼンタ色の記録液を調製した。

【0200】＜実施例9＞（マイクロカプセル化顔料中の顔料含有量が67%のマイクロカプセル化顔料分散液を使用した記録液の製造）

実施例7において、製造例2で得たフタロシアニンブルーのアニオン性マイクロカプセル化顔料含有水性分散液（MC-2）に代えて、製造例13で得たイエロー色のアニオン性マイクロカプセル化顔料含有水性分散液（MC-13）を使用した以外は、実施例7と同様にして、イエロー色の記録液を調製した。

【0201】＜実施例10＞（マイクロカプセル化顔料中の顔料含有量が75%のマイクロカプセル化顔料分散液を使用した記録液の製造）

製造例9で得たマゼンタ色のアニオン性マイクロカプセル化顔料含有水性分散液（MC-9）40.0部に、実施例7で使用了スチレンアクリル酸樹脂のアンモニア水溶液5.0部（樹脂固形分2.5部に相当）、エチレングリコール20部、ジエタノールアミン3.0部及びイオン交換水32.0部を混合して、顔料分が6%のマゼンタ色の記録液を調製した。

【0202】＜実施例11＞（マイクロカプセル化顔料中の顔料含有量が67%のマイクロカプセル化顔料分散液を使用した記録液の製造）

実施例7において、製造例2で得たフタロシアニンブルー

のアニオン性マイクロカプセル化顔料含有水性分散液（MC-2）に代えて、製造例4で得たフタロシアニンブルーのアニオン性マイクロカプセル化顔料含有水性分散液（MC-4）を使用した以外は、実施例7と同様にして、シアン色の記録液を調製した。

【0203】実施例7、8、9、10及び11において、記録液を調製するに当たっては、特にビーズミルやロール等の分散機を必要とせず、単に混合するのみで調製できたので、分散設備が不要で、分散工程や労力を短縮でき、製造時間の短縮あるいは分散エネルギーの省力化ができ、生産性を大きく上げるとともに製造コストの削減することができた。また、これらに使用したアニオン性マイクロカプセル化顔料含有水性分散液は、アニオン性マイクロカプセル化顔料中の顔料分が67%以上と高く、また、水性分散液中の顔料分も13.4%以上と高く、記録液としての性能を上げるために使用される水溶性樹脂や水溶性有機溶剤等の他の材料をかなりの量で添加可能であり、汎用性が高かった。

【0204】これらシアン色、マゼンタ色、イエロー色の記録液中のマイクロカプセル化顔料の体積平均粒子径及び30日間室温で貯蔵した後の体積平均粒子径及び粒子の沈降性を表5に示した。本実施例の記録液中のアニオン性マイクロカプセル化顔料の体積平均粒子径は、貯蔵前後でほぼ同等の値を示し、さらに粒子の沈降が見られず、従来のマイクロカプセル化顔料に比べ、貯蔵安定性及び分散安定性に非常に優れていることが明らかである。

【0205】次に、上記記録液を用いて、市販のピエゾ方式のインクジェットプリンターを用いて、シアン色、マゼンタ色及びイエロー色のカラー記録画像を、OHPシート及びコピー紙に記録した。この記録画像は、表6及び7に示したように、精細度や色濃度が高く、演色性や透明性に優れていた。また、OHPシートに記録した画像は、透明性に優れているためにカラフルな投影図を示していた。OHPシート上の記録画像を水をつけて擦っても消えることがなく、耐水性にも優れていた。また、繰り返し使用しても、インクを吐出させるノズルが詰まることもなかった。

【0206】＜比較例2＞（マイクロカプセル化顔料中の顔料含有量が33%のマイクロカプセル化顔料分散液を使用した記録液の製造）

製造例10で得たマゼンタ色のアニオン性マイクロカプセル化顔料含有水性分散液（MC-10）90.1部に、実施例7で使用了スチレンアクリル酸樹脂のアンモニア水溶液5.0部（樹脂固形分2.5部に相当）、エチレングリコール1.9部及びジエタノールアミン3.0部を混合して、顔料分が6%のマゼンタ色の記録液を調製した。

【0207】これに使用したアニオン性マイクロカプセル化顔料含有水性分散液は、アニオン性マイクロカプセル

ル化顔料中の顔料分が3.3%と低く、また、水性分散液中の顔料分も6.6%と低く、記録液の色濃度を保ったまま、記録液としての性能を上げるために使用される水溶性樹脂や水溶性有機溶剤等の他の材料の添加量に限りがあり、汎用性に欠けるものであった。また、マイクロカプセルに使用される樹脂量が多いために、他の材料との相溶性に問題が生じた。

【0208】このマゼンタ色の記録液中のマイクロカプセル化顔料の体積平均粒子径及び30日間室温で貯蔵した後の体積平均粒子径及び粒子の沈降性を表8に示した。本比較例の記録液中のアニオン性マイクロカプセル化顔料の体積平均粒子径は、貯蔵前後でほぼ同等の値を示し、さらに粒子の沈降が見られず、貯蔵安定性及び分散安定性に非常に優れていた。

【0209】次に、上記記録液を用いて、市販のピエゾ方式のインクジェットプリンターを用いて、マゼンタ色のカラー記録画像を、OHPシート、コピー紙に記録した。記録液中のエチレングリコールの添加量が少ないうえに、コピー紙やOHPシートに対して滲みや弾きを生じ、その記録画像は、表9に示すように、精細度が低く、演色性や透明性に欠けていた。また、OHPシートに記録した画像は、不透明でカラフルな投影図を示さず、OHPシートには使用できなかった。OHPシート上の記録画像を水をつけて擦っても消えることはなく、耐水性には優れていた。また、繰り返し使用した場合、インクを吐出させるノズルが詰まることもあった。

【0210】＜比較例3＞（マイクロカプセル化顔料中の顔料含有量が8.3%のマイクロカプセル化顔料分散液を使用した記録液の製造）

製造例8で得たマゼンタ色のアニオン性マイクロカプセル化顔料含有水性分散液（MC-8）3.6.1部に、実施例7で使用したスチレンアクリル酸樹脂のアンモニア水溶液5.0部（樹脂固形分2.5部に相当）、エチレングリコール20部、ジエタノールアミン3.0部及びイオン交換水35.9部を混合して、顔料分が6%のマゼンタ色の記録液を調製した。

【0211】このマゼンタ色の記録液中のマイクロカプセル化顔料の体積平均粒子径及び30日間室温で貯蔵した後の体積平均粒子径及び粒子の沈降性を表8に示した。本比較例の記録液中のアニオン性マイクロカプセル化顔料は、樹脂濃度が低いために顔料を微細な状態で安定に保つことができず、アニオン性マイクロカプセル化顔料は貯蔵後凝集を起こし、体積平均粒子径が大きくなり、粒子の沈降も見られ、貯蔵安定性及び分散安定性が悪かった。

【0212】次に、上記記録液を用いて、市販のピエゾ方式のインクジェットプリンターを用いて、マゼンタ色のカラー記録画像を、OHPシート、コピー紙に記録した。カプセルが凝集を起こしているため、この記録画像は、表9に示すように、精細度や色濃度が低く、演色性

や透明性に欠けていた。また、OHPシートに記録した画像は、不透明でカラフルな投影図を示さず、OHPシートには使用できなかった。また、繰り返し使用しているうちに、インクを吐出させるノズルが詰まり、プリンターの使用ができなくなった。

【0213】＜比較例4＞（マイクロカプセル化顔料の平均粒子径が650nmで最大粒子径が1000nmを越えるマイクロカプセル化顔料分散液を使用した記録液の製造）

製造例5で得たフタロシアニンブルーのアニオン性マイクロカプセル化顔料含有水性分散液（MC-5）4.4.8部に、実施例7で使用したスチレンアクリル酸樹脂のアンモニア水溶液5.0部（樹脂固形分2.5部に相当）、エチレングリコール20部、ジエタノールアミン3.0部及びイオン交換水27.2部を混合して、顔料分が6%のシアン色の記録液を調製した。

【0214】このシアン色の記録液中のマイクロカプセル化顔料の体積平均粒子径及び30日間室温で貯蔵した後の体積平均粒子径及び粒子の沈降性を表8に示した。本比較例の記録液中のアニオン性マイクロカプセル化顔料の体積平均粒子径は、貯蔵前後でほぼ同等の値を示したが、粒子の沈降が見られ、貯蔵安定性及び分散安定性が悪かった。

【0215】次に、上記記録液を用いて、市販のピエゾ方式のインクジェットプリンターを用いて、シアン色のカラー記録画像を、OHPシート、コピー紙に記録した。この記録画像は、表9に示すように、精細度や色濃度が低く、演色性や透明性に欠けていた。また、OHPシートに記録した画像は、不透明でカラフルな投影図を示さず、OHPシートには使用できなかった。また、繰り返し使用しているうちに、インクを吐出させるノズルが詰まり、プリンターの使用ができなくなった。

【0216】＜比較例5＞（有機顔料の平均粒子径が200nmを越えるマイクロカプセル化顔料分散液を使用した記録液の製造）

製造例11で得たマゼンタ色のアニオン性マイクロカプセル化顔料含有水性分散液（MC-11）4.4.8部に、実施例7で使用したスチレンアクリル酸樹脂のアンモニア水溶液5.0部（樹脂固形分2.5部に相当）、エチレングリコール20部、ジエタノールアミン3.0部及びイオン交換水27.2部を混合して、顔料分が6%のマゼンタ色の記録液を調製した。

【0217】このマゼンタ色の記録液中のマイクロカプセル化顔料の体積平均粒子径及び30日間室温で貯蔵した後の体積平均粒子径及び粒子の沈降性を表8に示した。本比較例の記録液中のアニオン性マイクロカプセル化顔料の体積平均粒子径は、貯蔵前後でほぼ同等の値を示し、粒子の沈降が見られず、貯蔵安定性及び分散安定性に優れていた。

【0218】次に、上記記録液を用いて、市販のピエゾ

方式のインクジェットプリンターを用いて、マゼンタ色のカラー記録画像を、OHPシート、コピー紙に記録した。この記録画像は、表9に示すように、精細度や色濃度が低く、演色性や透明性に欠けていた。特に、OHPシートに記録した画像は、不透明でカラフルな投影図を示さず、OHPシートには使用できなかった。また、繰り返し使用しても、インクを吐出させるノズルが詰まることはなかった。

【0219】＜比較例6＞（有機顔料の平均粒子径が200nmを越えるマイクロカプセル化顔料分散液を使用した記録液の製造）

製造例14で得たイエロー色のアニオン性マイクロカプセル化顔料含有水性分散液（MC-14）4.4部、8部に、実施例7で使用したスチレンアクリル酸樹脂のアンモニア水溶液5.0部（樹脂固形分2.5部に相当）、エチレングリコール20部、ジエタノールアミン3.0部及びイオン交換水27.2部を混合して、顔料分が6%のイエロー色の記録液を調製した。

【0220】このイエロー色の記録液中のマイクロカプセル化顔料の体積平均粒子径及び30日間室温で貯蔵した後の体積平均粒子径及び粒子の沈降性を表8に示した。本比較例の記録液中のアニオン性マイクロカプセル化顔料の体積平均粒子径は、貯蔵前後でほぼ同等の値を示し、粒子の沈降が見られず、貯蔵安定性及び分散安定性に優れていた。

【0221】次に、上記記録液を用いて、市販のピエゾ方式のインクジェットプリンターを用いて、マゼンタ色のカラー記録画像を、OHPシート、コピー紙に記録した。この記録画像は、表9に示すように、精細度や色濃度が低く、演色性や透明性に欠けていた。特に、OHPシートに記録した画像は、不透明でカラフルな投影図を示さず、OHPシートには使用できなかった。また、繰り返し使用しても、インクを吐出させるノズルが詰まることはなかった。

【0222】＜実施例12＞（不揮発性の塩基のマイクロカプセル化顔料分散液を使用した記録液の製造）  
製造例15で得たフタロシアニンブルーのアニオン性マイクロカプセル化顔料含有水性分散液（MC-15）37.5部に、エチレングリコール5部、グリセリン10.0部、ジエタノールアミン3.0部及びイオン交換水44.5部を混合して、顔料分が5.0%のシアン色の記録液を調製した。

【0223】＜実施例13＞（不揮発性の塩基のマイクロカプセル化顔料分散液を使用した記録液の製造）  
実施例12において、製造例15で得たフタロシアニンブルーのアニオン性マイクロカプセル化顔料含有水性分散液（MC-15）に代えて、製造例16で得たマゼンタ色のアニオン性マイクロカプセル化顔料含有水性分散液（MC-16）を用いた以外は、実施例12と同様にして、マゼンタ色の記録液を調製した。

【0224】＜実施例14＞（不揮発性の塩基のマイクロカプセル化顔料分散液を使用した記録液の製造）

実施例12において、製造例15で得たフタロシアニンブルーのアニオン性マイクロカプセル化顔料含有水性分散液（MC-15）に代えて、製造例17で得たイエロー色のアニオン性マイクロカプセル化顔料含有水性分散液（MC-17）を用いた以外は、実施例12と同様にして、イエロー色の記録液を調製した。

【0225】実施例12、13及び14において、記録液を調製するに当たっては、特にビーズミルやロール等の分散機を必要とせず、単に混合するのみで調製できたので、分散設備が不要で、分散工程や労力を短縮でき、製造時間の短縮あるいは分散エネルギーの省力化ができ、生産性を大きく上げるとともに製造コストの削減することができた。また、これらに使用したアニオン性マイクロカプセル化顔料含有水性分散液は、アニオン性マイクロカプセル化顔料中の顔料分が6.7%と高く、また、水性分散液中の顔料分も13.4%以上と高く、記録液としての性能を上げるために使用される水溶性樹脂や水溶性有機溶剤等の他の材料をかなりの量で添加可能であり、汎用性が高かった。

【0226】次に、これらシアン色、マゼンタ色及びイエロー色の記録液中のマイクロカプセル化顔料の体積平均粒子径及び30日間室温で貯蔵した後の体積平均粒子径及び粒子の沈降性を表5に示した。実施例12、13及び14で得た各記録液中のアニオン性マイクロカプセル化顔料の体積平均粒子径は、貯蔵前後でほぼ同等の値を示し、さらに粒子の沈降が見られず、従来のマイクロカプセル化顔料に比べ、貯蔵安定性及び分散安定性に非常に優れていることが明らかである。

【0227】次に、上記記録液を用いて、市販のピエゾ方式のプリンターを用いて、シアン色、マゼンタ色及びイエロー色のカラー記録画像を、OHPシート及びコピー紙に記録した。これらの記録画像は、表7に示すように、精細度や色濃度が高く、演色性や透明性に優れていた。また、この記録画像は、透明性に優れているためにカラフルな投影図を示していた。さらに、OHPシート上の記録画像を水をつけて擦ると消えやすいが、コピー紙上の記録画像に、水を数滴垂らしても、滲んで記録画像が見えなくなることはなく、耐水性にも優れていた。

【0228】また、これらのシアン色、マゼンタ色及びイエロー色のインクを詰めたノズルを室温で15日間放置した後、クリーニングして使用した場合、揮発性のアミンを使用した場合に比べて、クリーニング回数が3回以内で済むことから、インクの再分散性に非常に優れていた。

【0229】＜実施例15＞（ゲル化処理したマイクロカプセル化顔料分散液を使用した記録液の製造）  
製造例18で得たカーボンブラックのアニオン性マイク



ロカプセル化顔料含有水性分散液 (MC-18) 37.5 部に、エチレングリコール 5 部、グリセリン 10.0 部、ジエタノールアミン 3.0 部及びイオン交換水 44.5 部を混合して、顔料分が 5.0 % のカーボンブラックの記録液を調製した。

【0230】次に、このカーボンブラックの記録液中のマイクロカプセル化顔料の体積平均粒子径及び 30 日間室温で貯蔵した後の体積平均粒子径及び粒子の沈降性を表 5 に示した。この記録液中のアニオン性マイクロカプセル化顔料の体積平均粒子径は、貯蔵前後でほぼ同等の値を示し、さらに粒子の沈降が見られず、従来のマイクロカプセル化顔料に比べ、貯蔵安定性及び分散安定性に非常に優れていることが明らかである。

【0231】次に、上記記録液を用いて、市販のピエゾ方式のインクジェットプリンターを用いて、ブツラ色の記録画像を、OHP シート及びコピー紙に記録した。これらの記録画像は、表 7 に示すように、漆黒みがあり、精細度や色濃度が高かった。さらに、OHP シート上の記録画像を水をつけて擦るっても消えにくく、耐水性にも優れていた。

【0232】また、この記録液を詰めたノズルを室温で 15 日間放置した後、クリーニングして使用した場合、クリーニング回数が 6 回で済むことから、インクの再分散性にも優れていた。

【0233】さらに、この記録液をガラスビンに入れ密閉し、80℃で 10 日間高温槽で耐溶剤性試験を行なったところ、体積平均粒子径が 189 nm と試験前と比べて変化がなく凝集することなく非常に優れていた。

【0234】＜実施例 16＞（不揮発性の塩基のマイクロカプセル化顔料分散液を使用した記録液の製造）

製造例 3 で得たフタロシアニンブルーのアニオン性マイクロカプセル化顔料含有水性分散液 (MC-3) 44.8 部に、実施例 7 で使用したスチレンアクリル酸樹脂のアンモニア水溶液 5.0 部（樹脂固形分 2.5 部に相当）、エチレングリコール 20 部、ジエタノールアミン 3.0 部及びイオン交換水 27.2 部を混合して、顔料分が 6 % のシアン色の記録液を調製した。

【0235】このシアン色の記録液中のマイクロカプセル化顔料の体積平均粒子径及び 30 日間室温で貯蔵した後の体積平均粒子径及び粒子の沈降性を表 5 に示した。本比較例の記録液中のアニオン性マイクロカプセル化顔料の体積平均粒子径は、貯蔵前後でほぼ同等の値を示し、粒子の沈降が見られず、貯蔵安定性及び分散安定性に優れていた。

【0236】次に、上記記録液を用いて、市販のピエゾ方式のインクジェットプリンターを用いて、シアン色のカラー記録画像を、OHP シート、コピー紙に記録した。この記録画像は、表 7 に示すように、精細度や色濃度が高く、演色性や透明性に優れていた。特に、OHP シートに記録した画像は、透明でカラフルな投影図を示した。さらに、OHP シート上の記録画像を水をつけて擦ると消えやすいが、コピー紙上の記録画像に、水を数滴垂らしても、滲んで記録画像が見えなくなることはなく、耐水性にも優れていた。

【0237】また、このシアン色の記録液を詰めたノズルを室温で 15 日間放置した後、クリーニングして使用した場合、クリーニング回数が 3 回以内で済むことから、インクの再分散性に非常に優れていた。

【0238】

【表 4】

	マイクロカプセル化顔料含有水性分散液	体積平均径(nm)		沈降性
		貯蔵前	貯蔵後	
実施例1	MC-2	175	180	○
実施例2	MC-7	182	186	○
実施例3	MC-13	192	190	○
実施例4	MC-1	152	155	○
実施例5	MC-6	143	148	○
実施例6	MC-12	182	179	○
実施例7	MC-2	176	183	○
実施例8	MC-7	173	172	○
実施例9	MC-13	183	192	○
実施例10	MC-9	185	189	○

【0239】

【表5】

	マイクロカプセル化顔料含有水性分散液	体積平均径(nm)		沈降性
		貯蔵前	貯蔵後	
実施例11	MC-4	225	221	○
実施例12	MC-15	158	154	○
実施例13	MC-16	182	174	○
実施例14	MC-17	188	193	○
実施例15	MC-18	153	147	○
実施例16	MC-3	172	171	○

【0240】表4及び5における略号、評価方法及び評価基準は以下の通りである。

体積平均径 : アニオン性マイクロカプセル化顔料の体積平均粒子径 (nm)

沈降性 : 貯蔵後の粒子の沈降状態

○=良好

×=沈降がみられる

【0241】

【表6】

	マイクロ カプセル 化顔料 含有水性 分散液	ジェット プリンタ の種類	再 分 散 性	記 録 画 像			
				耐 水 性	精 細 度	色 濃 度	透 明 性
実施例 1	MC-2	B J	—	○	○	○	○
実施例 2	MC-7	B J	—	○	○	○	○
実施例 3	MC-13	B J	—	○	○	○	○
実施例 4	MC-1	P J	△	○	○	○	○
実施例 5	MC-6	P J	△	○	○	○	○
実施例 6	MC-12	P J	△	○	○	○	○
実施例 7	MC-2	P J	△	○	○	○	○
実施例 8	MC-7	P J	△	○	○	○	○
実施例 9	MC-13	P J	△	○	○	○	○
実施例10	MC-9	P J	△	○	○	○	○

【0242】

【表7】

	マイクロ カプセル 化顔料 含有水性 分散液	ジェット プリンタ の種類	再 分 散 性	記 録 画 像			
				耐 水 性	精 細 度	色 濃 度	透 明 性
実施例11	MC-4	P J	△	○	○	○	○
実施例12	MC-15	P J	○	△	○	○	○
実施例13	MC-16	P J	○	△	○	○	○
実施例14	MC-17	P J	○	△	○	○	○
実施例15	MC-18	P J	△	○	○	○	—
実施例16	MC-3	P J	○	△	○	○	○

【0243】表6及び7における略号、評価方法及び評価基準は、以下の通りである。

B J : バブルジェット方式のインクジェットプリンター

P J : ピエゾ方式のインクジェットプリンター

再分散性 : インクを充填したまま室温で 15 日間室内に放置後、再度印字するしやすさにより評価する。

○=クリーニングが 3 回以内で印字可能

△=クリーニングが 4~9 回

×=10 回以上

— : 未評価

耐水性 : ○=OHP シートでも消えない

△=コピー紙で滲みが少ない

×=コピー紙で滲み記録画像が読めない

精細度 : ○=良好

×=悪い

色濃度 : ○=高い

×=低い

透明性 : ○=透明

×=不透明

【0244】

【表 8】

	マイクロカプセル化顔料含有水性分散液	体積平均径 (nm)		沈降性
		貯蔵前	貯蔵後	
比較例 1	MC-5	570	581	×
比較例 2	MC-7	230	235	○
比較例 3	MC-13	735	1259	×
比較例 4	MC-5	690	770	×
比較例 5	MC-1	290	307	○
比較例 6	MC-6	257	265	○

【0245】表 8 における略号、評価方法及び評価基準は以下の通りである。

体積平均径 : アニオン性マイクロカプセル化顔料の体積平均粒子径 (nm)

沈降性 : 貯蔵後の粒子の沈降状態

○=良好

×=沈降がみられる

【0246】

【表 9】

	マイクロ カプセル 化顔料 含有水性 分散液	ジェット プリンタ の種類	再 分 散 性	記 録 画 像			
				耐 水 性	精 細 度	色 濃 度	透 明 性
比較例 1	MC-5	BJ	—	—	×	×	×
比較例 2	MC-10	PJ	—	○	×	×	×
比較例 3	MC-8	PJ	—	—	×	×	×
比較例 4	MC-5	PJ	—	—	×	×	×
比較例 5	MC-11	PJ	—	—	×	×	×
比較例 6	MC-14	PJ	—	—	×	×	×

【0247】表9における略号、評価方法及び評価基準は、以下の通りである。

BJ : バブルジェット方式のインクジェットプリンター

PJ : ピエゾ方式のインクジェットプリンター

再分散性 : インクを充填したまま室温で15日間室内に放置後、再度印字するしやすさにより評価する。

○=クリーニングが3回以内で印字可能

△=クリーニングが4～9回

×=10回以上

— : 未評価

耐水性 : ○=OHPシートでも消えない

△=コピー紙で滲みが少ない

×=コピー紙で滲み記録画像が読めない

精細度 : ○=良好

×=悪い

色濃度 : ○=高い

×=低い

透明性 : ○=透明

×=不透明

【0248】

【発明の効果】本発明の記録液用アニオン性マイクロカプセル化顔料含有水性分散液は、非常に細かい顔料分散体で、かつ、貯蔵安定性に優れているので、精細度や色濃度が高く、演色性や透明性に優れ、分散工程の省力化により、製造コストと記録液のコストの低減が図れる。また、本発明の記録液用アニオン性マイクロカプセル化

顔料含有水性分散液は、顔料分が高いので、記録液に加工する際に、処方上、種々の材料が使用できる余裕があり、汎用性が高いという利点がある。

【0249】さらに、不揮発性の塩基を使用することにより再分散性に優れることから、記録液の信頼性が高まるという利点がある。

【公報種別】特許法第 17 条の 2 の規定による補正の掲載  
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【手続補正書】  
 【提出日】平成 15 年 8 月 25 日 (2003. 8. 25)  
 【手続補正 1】  
 【補正対象書類名】明細書  
 【補正対象項目名】特許請求の範囲  
 【補正方法】変更  
 【補正の内容】  
 【特許請求の範囲】  
 【請求項 1】

有機顔料又はカーボンブラックをアニオン性基含有有機高分子化合物類で被覆して成るアニオン性マイクロカプセル化顔料含有水性分散液であって、アニオン性マイクロカプセル化顔料中の有機顔料又はカーボンブラックの含有割合が 35～80 重量%の範囲にあることを特徴とする記録液用水性分散液。

【請求項 2】

アニオン性マイクロカプセル化顔料の最大粒子径が 1000 nm 以下で、かつ平均粒子径が 300 nm 以下である請求項 1 記載の記録液用水性分散液。

【請求項 3】

最大粒子径が 200 nm 以下で、かつ一次粒子の平均粒子径が 10～100 nm の範囲にある有機顔料又はカーボンブラックを含有するアニオン性マイクロカプセル化顔料であることを特徴とする請求項 1 又は 2 記載の記録液用水性分散液。

【請求項 4】

硬化剤及び／又は高分子化合物と有機顔料とをアニオン性基含有有機高分子化合物類で被覆したアニオン性マイクロカプセル化顔料を含有することを特徴とする請求項 1、2 又は 3 記載の記録液用水性分散液。

【請求項 5】

アニオン性基含有有機高分子化合物類及び、有機顔料又はカーボンブラックを含有する有機溶剤相に水を投入することにより得られるアニオン性マイクロカプセル化顔料を用いる請求項 1、2又は3記載の記録液用水性分散液。

【請求項 6】

アニオン性基含有有機高分子化合物類、有機顔料又はカーボンブラック、及び硬化剤及び／又は高分子化合物を含有する有機溶剤相に水を投入することにより得られるアニオン性マイクロカプセル化顔料を用いる請求項 4 記載の記録液用水性分散液。

【請求項 7】

アニオン性基含有有機高分子化合物類及び、有機顔料又はカーボンブラックを含有する有機溶剤相に超音波を照射しながら水を投入することにより得られるアニオン性マイクロカ



プセル化顔料を用いる請求項 5 又は 6 記載の記録液用水性分散液。

【請求項 8】

アニオン性基含有有機高分子化合物類及び、有機顔料又はカーボンブラックを含有する有機溶剤相を水中に投入することにより得られるアニオン性マイクロカプセル化顔料を用いる請求項 1、2 又は 3 記載の記録液用水性分散液。

【請求項 9】

アニオン性基含有有機高分子化合物類、有機顔料又はカーボンブラック、及び硬化剤及び／又は高分子化合物を含有する有機溶剤相を水中に投入することにより得られるアニオン性マイクロカプセル化顔料を用いる請求項 4 記載の記録液用水性分散液。

【請求項 10】

アニオン性基含有有機高分子化合物類及び、有機顔料又はカーボンブラックからなる含水ケーキを、塩基性化合物を用いてアニオン性基の一部又はすべてを中和させることにより得られるアニオン性マイクロカプセル化顔料を用いる請求項 1、2、3 又は 4 記載の記録液用水性分散液。

【請求項 11】

アニオン性基含有有機高分子化合物類のアニオン性基の一部又はすべてを塩基性化合物をもって中和し、有機顔料又はカーボンブラックと、水性媒体中で混練する工程、及び、酸性化合物をもって pH を中性又は酸性にしてアニオン性基含有有機高分子化合物類を析出させて顔料に固着する工程とからなる製法によって得られる含水ケーキを使用する請求項 8 又は 9 記載の記録液用水性分散液。

【請求項 12】

請求項 1、2、3、4、5、6、7、8、9、10 又は 11 記載の記録液用水性分散液を含有する記録液。

【請求項 13】

インクジェットプリンター用である請求項 12 記載の記録液。

## PATENT ABSTRACTS OF JAPAN

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(21)Application number : 08-228327 (71)Applicant : DAINIPPON INK & CHEM INC  
(22)Date of filing : 29.08.1996 (72)Inventor : TAKAO NAGAYUKI  
ASADA MASAHIKO  
SAITO NAOTO

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(54) AQUEOUS DISPERSION FOR RECORDING LIQUID CONTAINING ANIONIC  
MICROENCAPSULATED PIGMENT AND RECORDING LIQUID

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain the subject dispersion liquid produced by coating an organic pigment or carbon black with a prescribed amount of an organic polymer compound having anionic group, giving excellent fineness and color density, having excellent color rendering property and transparency and useful for water-based ball-pointed pen, etc.

SOLUTION: This dispersion is produced by coating (A) an organic pigment or (B) carbon black with (C) an organic polymer compound having anionic group (e.g. organic amine salt) and contains 35-80wt.% of the component A or the component B. Preferably, the maximum particle diameter of the primary particle of the component A or the component B is  $\leq 200\text{nm}$  and the average particle diameter is 10-100nm. The maximum particle diameter of the produced anionic microencapsulated pigment is  $\leq 1,000\text{nm}$  and the average particle diameter is  $\leq 300\text{nm}$ . The dispersion may be incorporated with a curing agent and/or a polymer.

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CLAIMS

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## [Claim(s)]

[Claim 1] the recording ink characterized by being in the range the organic pigment in an anionic microencapsulation pigment or whose content rate of carbon black it is anionic microencapsulation pigment content aqueosity dispersion liquid which cover an organic pigment or carbon black with anionic radical content organic high molecular compounds, and change, and is 35 - 80 % of the weight -- service water -- sex dispersion liquid.

[Claim 2] Aqueosity dispersion liquid for recording ink according to claim 1 whose mean particle diameter the maximum particle diameter of an anionic microencapsulation pigment is 1000nm or less, and is 300nm or less.

[Claim 3] Aqueosity dispersion liquid for recording ink according to claim 1 or 2 characterized by for the maximum particle diameter being 200nm or less, and being an anionic microencapsulation pigment containing the organic pigment or carbon black in the range whose mean particle diameter of a primary particle is 10-100nm.

[Claim 4] Aqueosity dispersion liquid for recording ink according to claim 1, 2, or 3 characterized by containing the anionic microencapsulation pigment which covered the curing agent and/or the high molecular compound, and the organic pigment with anionic radical content organic high molecular compounds.

[Claim 5] Aqueosity dispersion liquid for recording ink according to claim 1, 2, 3, or 4 whose anionic radical content organic high molecular compounds are organic amine salts.

[Claim 6] Aqueosity dispersion liquid for recording ink according to claim 1, 2, 3, or 4 whose anionic radical content organic high molecular compounds are alkali-metal salts.

[Claim 7] Aqueosity dispersion liquid for recording ink according to claim 1, 2, 3, 4, 5, or 6 whose acid number of anionic radical content organic high molecular compounds is 30 or more KOHmg/g.

[Claim 8] Aqueosity dispersion liquid for recording ink according to claim 7 whose anionic radical is a carboxyl group.

[Claim 9] Aqueosity dispersion liquid for recording ink according to claim 7 or 8 whose number average molecular weight of anionic radical content organic high molecular compounds is 2000 or more.

[Claim 10] Aqueosity dispersion liquid for recording ink according to claim 1, 2, 3, 5, 6, 7, 8, or 9 using the anionic microencapsulation pigment obtained by throwing water into the organic solvent phase containing anionic radical content organic high molecular compounds and an organic pigment, or carbon black.

[Claim 11] Aqueosity dispersion liquid for recording ink according to claim 4, 5, 6, 7, 8, or 9 using the anionic microencapsulation pigment obtained by throwing water into the organic solvent phase containing anionic radical content organic high molecular compounds, an organic pigment or carbon black and a curing agent, and/or a high molecular compound.

[Claim 12] Aqueosity dispersion liquid for recording ink according to claim 10 or 11 using the anionic microencapsulation pigment obtained by throwing in water, irradiating a supersonic wave at the organic solvent phase containing anionic radical content organic high molecular compounds and an organic pigment, or carbon black.

[Claim 13] Aqueosity dispersion liquid for recording ink according to claim 1, 2, 3, 5, 6, 7, 8, or 9 using the anionic microencapsulation pigment obtained by supplying the organic solvent phase containing anionic radical content organic high molecular compounds and an organic pigment, or carbon black underwater.

[Claim 14] Aqueosity dispersion liquid for recording ink according to claim 4, 5, 6, 7, 8, or 9 using the anionic microencapsulation pigment obtained by supplying the organic solvent phase containing anionic radical content organic high molecular compounds, an organic pigment or carbon black and a curing agent, and/or a high molecular compound underwater.

[Claim 15] Aqueosity dispersion liquid for recording ink according to claim 1, 2, 3, 4, 5, 6, 7, 8, or 9 using the anionic microencapsulation pigment obtained by neutralizing all the anionic all [ a part or ] using a

basic compound in the water cake which consists of anionic radical content organic high molecular compounds and an organic pigment, or carbon black.

[Claim 16] Aquosity dispersion liquid for recording ink according to claim 13 or 14 which use the water cake obtained by the process which neutralizes that a basic compound is also in all the anionic all [ a part or ] of anionic radical content organic high molecular compounds, and consists of a process kneaded an organic pigment or carbon black, and in an aquosity medium, and a process which pH is carried out to an acid compound being at neutrality or acidity, and anionic radical content organic high molecular compounds are deposited, and fixes to a pigment.

[Claim 17] recording ink claims 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, and 15 or given in 16 – service water – the recording ink containing sex dispersion liquid.

[Claim 18] Recording ink according to claim 17 which is an object for ink jet printers.

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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[Field of the Invention] the recording ink containing an anionic microencapsulation pigment with the high pigment concentration in a microencapsulation pigment useful as an ingredient for this invention to manufacture the aquosity recording ink for ink jet printers on demand type [, such as writing implements, such as an aquosity ball-point, a fountain pen, an aquosity felt-tipped marker, and an aquosity marker, Bubble Jet and a thermal jet method, and a piezo method, ] -- service water -- it is related with sex dispersion liquid and the recording ink containing the dispersion liquid.

[0002]

[Description of the Prior Art] Conventionally, the color has been used for the recording ink of which a high definition is required. Although the recording ink using a color has the descriptions, such as high transparency, a high definition, and outstanding color rendering properties, it has problems, such as lightfastness and a water resisting property.

[0003] In order to solve lightfastness and a waterproof problem in recent years, it replaces with a color and the recording ink using an organic pigment or carbon black is manufactured.

[0004] However, if distributed stabilization of the pigment is not carried out very finely when an organic pigment and carbon black are used, there is a trouble that a high definition and advanced color rendering properties cannot be acquired as recording ink. Especially, in the recording ink for ink jet printers, if distributed stabilization of the pigment is not carried out very finely, it will link with the trouble of the blinding of a nozzle directly. Moreover, if the pigment was distributed minutely and high transparency was not secured when an organic pigment was used for the application of the OHP sheet projected with a back light, there was a trouble that the projection image of colorful OHP was not obtained.

[0005] Compared with the organic pigments and carbon black which are generally used, such as a coating and ink, especially the organic pigment and carbon black that are used for these have a fine diameter of a primary particle, and since secondary condensation is strong, they need great energy for distributing these pigments even to a primary particle. Moreover, various devices are required to maintain the pigment in dispersion liquid at stability even if it is able to distribute these pigments to a primary particle.

[0006] In order to solve these troubles, as shown below, the approach of using a microcapsule is indicated. for example, to JP,62-95366,A To the approach and JP,1-170672,A which use for recording ink the microcapsule which connoted color ink in the polymer particle Make water dissolve or distribute coloring matter to an insoluble solvent substantially, and emulsification distribution of this is underwater

carried out using a surfactant. To the approach and JP,5-39447,A which use for recording ink the coloring matter which microencapsulated by the conventional technique The approach the endocyst object of a microcapsule uses water and the microcapsule which made the water-soluble solvent list dissolve or distribute a sublimability disperse dye to at least one sort of polyester resin for a record constituent, The water-color-ink constituent which becomes JP,6-313141,A from the colored emulsion-polymerization particle and various aquosity ingredients is indicated.

[0007]

[Problem(s) to be Solved by the Invention] However, it had the trouble that that of what encapsulated the color was inferior to lightfastness, and since the microencapsulation pigment manufactured by the conventional approach had a large particle size, it had the trouble of being inferior to transparency, color enhancement, color rendering properties, etc. Moreover, since the resin concentration in a capsule was high (pigment concentration is low), the selectivity of the ingredient used for recording ink was small, versatility was missing, and the recording ink had further the trouble that a feeling of concentration was lost. furthermore, the thing for which a detailed microencapsulation pigment is manufactured only by resin when pigment concentration is made high too much -- difficult -- so -- a surfactant -- not using together -- it was not that from which the record image with which it does not obtain, therefore is not necessarily satisfied of a water resisting property is obtained.

[0008] In manufacture of the recording ink with which the pigment dispersion liquid of a drainage system were used for the technical problem which this invention tends to solve Laborsaving of the process which distributes a pigment minutely on the dispersion-medium object of recording ink is realized, a great effort, a facility, energy, etc. are saved labor, and the microencapsulation pigment content aquosity dispersion liquid which can reduce the manufacturing cost of recording ink are offered, Moreover, the thing for which the microencapsulation pigment content aquosity dispersion liquid for recording ink with the high versatility excellent in the degree of freedom of selections, such as resin for recording ink, various additives, or a solvent, are offered, Furthermore, it is in offering the recording ink using a feeling of concentration, a high definition, the color rendering properties and transparency that are required of recording ink, and the microencapsulation pigment content aquosity dispersion liquid and these aquosity dispersion liquid for recording ink which were further excellent in a water resisting property, redispersible, etc.

[0009]

[Means for Solving the Problem] It is anionic microencapsulation pigment content aquosity dispersion liquid which cover an organic pigment or carbon black with anionic radical content organic high molecular compounds as a result of repeating examination, and change wholeheartedly that this invention persons should solve the above-mentioned technical problem. When the anionic microencapsulation pigment content aquosity dispersion liquid in the range the organic pigment in an anionic microencapsulation pigment or whose content of carbon black is 35 - 80 % of the weight are processed into recording ink, Since it can be used only by there being neither selection of the resin at the time of manufacture, a solvent, or various additives nor a limit of an addition, and versatility being raised, and mixing anionic microencapsulation pigment content aquosity dispersion liquid further, Since it is not necessary to carry out indispensable use of that reducing the conventional manufacturing cost, the definition of recording ink, and color rendering properties and transparency can be improved more than before, and the surfactant Raising the water resisting property of a record image, that raise redispersible and the dependability of recording ink is raised by using the thing (alkali metal) of a non-volatile for the base for neutralization of the anionic radical content organic high molecular compounds which are resin for microencapsulating further, etc. A header, It came to complete this invention.

[0010] In order that this invention may solve the above-mentioned technical problem, the need is accepted in an organic pigment or carbon black. Namely, with a curing agent and a high molecular compound Anionic radical content organic high molecular compounds (it abbreviates to "anionic organic

high molecular compounds" hereafter.) It is aqueous dispersion liquid containing the covered anionic microencapsulation pigment. The recording ink containing the anionic microencapsulation pigment content aqueous dispersion liquid for recording ink and these aqueous dispersion liquid which are characterized by being in the range the organic pigment in an anionic microencapsulation pigment or whose content of carbon black is 35 - 80 % of the weight is offered.

[0011] the recording ink containing the anionic microencapsulation pigment of this invention -- service water -- sex dispersion liquid The need is accepted in an organic pigment or carbon black. With a curing agent and a high molecular compound It covers with anionic organic high molecular compounds. Moreover, the content of the organic pigment or carbon black at 35 - 80 % of the weight Especially the thing whose mean particle diameter it is in the range whose mean particle diameter the maximum particle diameter of the primary particle of an organic pigment or carbon black is 200nm or less, and is 10-100nm, the maximum particle diameter of an anionic microencapsulation pigment is 1000nm or less, and is 300nm or less is desirable. Moreover, the thing of the form which neutralized anionic organic high molecular compounds by the base is desirable, and it is desirable to use especially alkali metal.

[0012] Furthermore, if the anionic microencapsulation pigment is the thing of the form which are the anionic organic high molecular compounds containing a curing agent and a high molecular compound, with covered the organic pigment, it is desirable much more.

[0013] Furthermore, other matter, such as a vehicle for titanium, the mineral matter like aluminum, a pigment derivative, a pigment agent, a pigment wetting agent, an organic solvent, a plasticizer, an ultraviolet ray absorbent, an anti-oxidant, or recording ink, can also be included into the capsule of the microencapsulation pigment of this invention again.

[0014]

[Embodiment of the Invention] As the manufacture approach of the anionic microencapsulation pigment contained in the aqueous dispersion liquid for recording ink of this invention, the two approaches of the physical and mechanical technique and the chemical technique, such as the coacervation method, interfacial polymerization, and the Inn SAICHU method, are mentioned as an approach from the former.

[0015] However, even if the particle size of the microencapsulation pigment obtained by these conventional-type approaches is the thing of the magnitude below submicron (micrometer) one, since particle diameter is large and the rate that the pigment in a microcapsule occupies is low, when recording ink is manufactured using this microencapsulation pigment, what can not necessarily be satisfied in the feeling of concentration of definition, color rendering properties, transparency, or a color is not obtained. Furthermore, it is necessary to manufacture a microencapsulation pigment with the rate for it to be detailed and high that the pigment in a microcapsule occupies.

[0016] Moreover, since the resin concentration in a capsule is high (pigment concentration is low), the ingredient used for recording ink is restricted, or in order to use a surfactant, a water resisting property is inferior.

[0017] As the manufacture approach of the anionic microencapsulation pigment contained in the aqueous dispersion liquid for recording ink of this invention Fundamentally a mixture (a composite or complex) with the anionic organic high molecular compounds which have self-dispersion power or dissolution ability to water, an organic pigment, or carbon black Or the approach of making a mixture with an organic pigment or carbon black, a curing agent, and an anionic organic high molecular compound an organic solvent phase, and throwing water into this organic solvent phase, or supplying this organic solvent phase underwater, and changing self-distribution (phase inversion emulsification) (it is hereafter called a "phase inversion method".) It is desirable.

[0018] It neutralizes that a basic compound is also in all the anionic all [ a part or ] of anionic radical content organic high molecular compounds. Or an organic pigment or carbon black, The water cake obtained by the process which consists of a process kneaded in an aqueous medium, and a process which pH is carried out to an acid compound being at neutrality or acidity, and anionic radical content

organic high molecular compounds are deposited, and fixes to a pigment How to acquire by neutralizing all the anionic all [ a part or ] using a basic compound (it is hereafter called the "\*\*\*\* method".) It is desirable.

[0019] By doing in this way, the aqueous dispersion liquid containing the anionic microencapsulation pigment of a high pigment content more detailed than the conventional approach of making it into the purpose can be manufactured.

[0020] Moreover, in the describing [ above ] phase inversion method, even if it makes the vehicle and additive for recording ink mix into an organic solvent phase and manufactures, it is satisfactory in any way. If it says from the ability of the dispersion liquid for direct recording ink to be manufactured especially, will make it more more desirable to mix the vehicle for recording ink.

[0021] The maximum particle diameter is 200nm or less, and the organic pigment or carbon black contained in the microcapsule of an anionic microencapsulation pigment has desirable organic pigment or carbon black in the range whose mean particle diameter of a primary particle is 10-100nm, in order to acquire the feeling of concentration of recording ink, transparency, and color rendering properties, or in order to manufacture a detailed microencapsulation pigment with a mean particle diameter of 300nm or less.

[0022] Although especially the class of organic pigment used by this invention is not limited, if it limits for illustrating a typical thing The Quinacridone system pigment, the Quinacridone quinone system pigment, a dioxazine system pigment, Phthalocyanine pigment, an anthra pyrimidine system pigment, an anthanthrone pigment, An indan SURON system pigment, a flavan SURON system pigment, a perylene system pigment, a diketopyrrolopyrrole pigment, A peri non system pigment, a kino FUTARON system pigment, an anthraquinone system pigment, a thioindigo system pigment, a Benz imidazolone system pigment, an isoindolinone system pigment, an azomethine system pigment, or azo pigment is mentioned.

[0023] Moreover, as for carbon black, neutrality, acidity, basic carbon, etc. are mentioned.

[0024] As a curing agent which may be contained with the pigment in the microcapsule of an anionic microencapsulation pigment For example, amino resin, such as melamine resin, benzoguanamine resin, and a urea-resin, Phenol resin, such as a TORIMECHI roll phenol and its condensate, tetramethylene di-isocyanate (TDI), Diphenylmethane diisocyanate (MDI), hexamethylene di-isocyanate (HDI), Naphthalene diisocyanate (NDI), isophorone diisocyanate (IPDI), The poly isocyanates, such as xylylene diisocyanate (XDI), those denaturation isocyanates, and blocked isocyanate, Fatty amine, aromatic amine, N-methyl piperazine, triethanolamine, Amines, such as a morpholine, dialkylamino ethanol, and benzyl dimethylamine, Polycarboxylic acid, phthalic anhydride, a maleic anhydride, anhydrous hexahydrophthalic acid, Acid anhydrides, such as pyromellitic dianhydride, anhydrous benzophenone tetracarboxylic acid, and ethylene glycol bis(trimellitate), The bisphenol A mold epoxy resin, a phenol system epoxy resin, a glycidyl methacrylate copolymer, Epoxy compounds, such as glycidyl ester resin of a carboxylic acid, and alicyclic epoxy, Polyether polyol, a polybutadiene glycol, the poly caprolactone polyol, Alcohols, such as tris hydroxyethyl isocyanate (THEIC), Vinyl compounds, such as a polyvinyl compound as a partial saturation radical content compound used for radical hardening or UV hardening by peroxide, or electron ray hardening, the Pori allyl compound, a glycol, and a reactant of polyol, an acrylic acid, or a methacrylic acid, etc. are mentioned.

[0025] As for these curing agents, it is more desirable to be used in order to harden the wall of an anionic microencapsulation pigment, or in order to raise the paint film reinforcement at the time of using it for recording ink, to add a photoinitiator, a polymerization initiator, or a catalyst, if still more nearly required, and to aim at promotion of hardening.

[0026] As a photoinitiator used for such the purpose, although benzoin, anthraquinone, benzophenones, \*\* sulfur compounds, dimethylbenzyl ketal, etc. are mentioned, it is not the object limited to these.

[0027] Similarly, as a polymerization initiator, \*\*\*\* azo compounds, such as \*\*\*\* peroxide; azobis isobutyl nitril, such as t-butyl peroxybenzoate, G t-butyl peroxide, cumene par hydroxide, acetyl peroxide, benzoyl peroxide, and lauroyl peroxide, azobis-2,4-dimethylvaleronitrile, and azobis cyclohexane carbonitrile, etc. are mentioned, for example.

[0028] Moreover, as a catalyst, Co compound, Pb compound, etc. are mentioned similarly, for example.

[0029] Although the high molecular compound which may be contained with the pigment in the microcapsule of an anionic microencapsulation pigment can be especially used without a limit if it is a with a number average molecular weight of 1,000 or more thing, the field of the film reinforcement of recording ink and the manufacture side of a capsule to its number average molecular weight is [ the thing of the range of 3,000-100,000 ] desirable.

[0030] Although especially the class of such a high molecular compound is not limited, for example A vinyl chloride, Polyvinyl systems, such as vinyl acetate, polyvinyl alcohol, and a polyvinyl butyral, Polyester systems, such as alkyd resin and phthalic resin, melamine resin, melamine formaldehyde resin, Amino systems, such as amino alkyd copolycondensation resin, a urea resin, and a urea-resin, thermoplasticity, High molecular compounds, such as the acrylic of thermosetting or denaturation, an epoxy system, a polyurethane system, a polyether system, a polyamide system, an unsaturated polyester system, a phenol system, a silicone system, and a fluorine system, those copolymers, or mixture is mentioned.

[0031] The anionic organic high molecular compounds used in order to manufacture an anionic microencapsulation pigment Although it has self-dispersion power or dissolution ability to water, and there will be no limit especially if it is anionic (acidity), in order to obtain what becomes enough as the capsule film or a paint film of recording ink Usually, the thing of the range of 1,000-100,000 has desirable number average molecular weight, and especially the thing of the range of 3,000-50,000 is desirable, and what dissolves in an organic solvent and serves as a solution is desirable.

[0032] Especially the self-dispersion power or dissolution ability of anionic organic high-molecular-compounds itself is given by neutralizing the anionic radical like the carboxyl group in the anionic organic high molecular compound concerned, a sulfonic acid group, or a phosphonic acid radical using alkali metal, such as ammonia, an organic amine like triethylamine, a sodium hydroxide and a potassium hydroxide, and a lithium hydroxide, for example, although not limited. Especially desirable self-dispersion power or dissolution ability is the thing of the form of making a carboxyl group introduce into these organic high molecular compounds, and being a base, with making it neutralize. In anionic organic high molecular compounds, you may have two or more sorts of these anionic radicals.

[0033] 30 or more KOHmg/g has the desirable acid number, and the amount of the carboxyl group in the anionic high molecular compounds which have a carboxyl group has the more desirable range used as 50-250. If the acid number of anionic high molecular compounds exceeds 250, since it is in the inclination for the storage stability of a capsule to be spoiled or for the water resisting property of a record image to fall remarkably, and a hydrophilic property will become high too much and it is in the inclination for the stability of a capsule to be spoiled or for particle diameter to become large when the acid number is lower than 30, it is not desirable.

[0034] As such anionic organic high molecular compounds For example, polyvinyl systems, such as a vinyl chloride, vinyl acetate, polyvinyl alcohol, and a polyvinyl butyral, Polyester systems, such as alkyd resin and phthalic resin, melamine resin, melamine formaldehyde resin, The ingredient of amino systems, such as amino alkyd copolycondensation resin, a urea resin, and a urea-resin; Thermoplasticity, The acrylic of thermosetting or denaturation, an epoxy system, a polyurethane system, The ingredient which has anionic radicals, such as a polyether system, a polyamide system, an unsaturated polyester system, a phenol system, a silicone system, fluorine system high molecular compounds, those copolymers, or mixture, is mentioned.

[0035] The anionic organic high molecular compounds used by this invention Although it has the



molecular weight which becomes enough as a capsule wallplate and actuation especially of the formation of wall formation is not needed, in order to make properties, such as the solvent resistance of a capsule wall, and endurance, improvement-ize further In order to raise the film reinforcement after film formation of recording ink, to or anionic organic high-molecular-compounds itself which is used beforehand By carrying out the pendant of the reactant active group like glycidyl group, isocyanate radical, hydroxyl-group or alpha, and beta-ethylene nature partial saturation double bond (vinyl group) Or by making photo-curing agents, such as the cross linking agent which has a reactant active group, for example, melamine resin, a urethane resin epoxy resin, an ethylene nature partial saturation monomer, and oligomer, etc. mix These reactant active groups, functional groups, etc. are used the time of formation of a capsule, or after formation or paint film formation of recording ink. It is more desirable to make the engine performance which is made to increase-ize, or constructs a bridge and gels the molecular weight of anionic organic high-molecular-compounds itself as an object for capsule wallplates give.

[0036] Among anionic organic high molecular compounds, further, anionic acrylic resin carries out the polymerization of these monomers and other monomers which may be copolymerized in a solvent to the acrylic monomer (it abbreviates to an anion radical content acrylic monomer hereafter) which has for example, an anionic radical, and is obtained with it if needed. Especially the acrylic monomer that the acrylic monomer which \*\* one or more anionic radicals chosen from the group which consists of a carboxyl group, a sulfonic group, and a HOSUHON radical as an anion radical content acrylic monomer, for example is mentioned, and has a carboxyl group also in these is desirable.

[0037] As an acrylic monomer which has a carboxy kill radical, an acrylic acid, a methacrylic acid, a crotonic acid, ethacrylic acid, a propyl acrylic acid, an isopropyl acrylic acid, an itaconic acid, boletic acid, etc. are mentioned, for example. An acrylic acid and a methacrylic acid are desirable also in these.

[0038] As an acrylic monomer which has a sulfonic group, sulfoethyl methacrylate, a butyl acrylamide sulfonic acid, etc. are mentioned, for example.

[0039] As an acrylic monomer which has a HOSUHON radical, phospho ethyl methacrylate etc. is mentioned, for example.

[0040] As an anion radical content acrylic monomer and other monomers which may be copolymerized For example, a methyl acrylate, an ethyl acrylate, acrylic-acid isopropyl, Acrylic-acid-n-propyl, acrylic-acid-n-butyl, acrylic-acid-t-butyl, 2-ethylhexyl acrylate, acrylic-acid-n-octyl, acrylic-acid lauryl, Acrylic-acid benzyl, a methyl methacrylate, ethyl methacrylate, methacrylic-acid isopropyl, Methacrylic-acid-n-propyl, n-butyl methacrylate, methacrylic-acid isobutyl, T-butyl methacrylate, 2-ethylhexyl methacrylate, n-octyl methacrylate, Methacrylic-acid lauryl, stearyl methacrylate, tridecyl methacrylate, \*\*\*\* (meta) acrylic ester [, such as methacrylic-acid benzyl, ]; -- addition reaction object [ of stearin acid, \*\*\*\*\* fatty acids, such as an addition reaction object of glycidyl methacrylate, and the acrylic ester monomer that has oxirane structure (meta) ]; -- a three or more carbon atomic numbers alkyl group The addition reaction object of the oxirane compound and acrylic acid (meta) which are included; Styrene, Alpha methyl styrene, o-methyl styrene, m-methyl styrene, p-methyl styrene, \*\*\*\* styrene system monomer [, such as p-tert-butyl styrene, ]; -- \*\*\*\* itaconic-acid ester [, such as itaconic-acid benzyl, ]; -- \*\*\*\* maleates [, such as maleic-acid dimethyl, ]; -- \*\*\*\* boletic acid ester [, such as boletic acid dimethyl, ]; -- acrylonitrile and a methacrylonitrile -- Vinyl acetate, acrylic-acid isobornyl, methacrylic-acid isobornyl, Acrylic-acid aminoethyl, acrylic-acid aminopropyl, methyl-acrylate aminoethyl, Acrylic-acid methylaminopropyl, ethyl-acrylate aminoethyl, Acrylic-acid ethylaminopropyl, an acrylic-acid aminoethyl amide, An acrylic-acid aminopropyl amide, a methyl-acrylate aminoethyl amide, An acrylic-acid methylaminopropyl amide, an ethyl-acrylate aminoethyl amide, An acrylic-acid ethylaminopropyl amide, a methacrylic-acid amide, methacrylic-acid aminoethyl, Methacrylic-acid aminopropyl, methyl-methacrylate aminoethyl, methacrylic-acid methylaminopropyl, Ethyl methacrylate aminoethyl, methacrylic-acid ethylaminopropyl, A methacrylic-acid aminoethyl amide, a methacrylic-acid

aminopropyl amide, A methyl-methacrylate aminoethyl amide, a methacrylic-acid methylaminopropyl amide, An ethyl methacrylate aminoethyl amide, a methacrylic-acid ethylaminopropyl amide, Acrylic-acid hydroxymethyl, acrylic-acid-2-hydroxyethyl, 2-hydroxypropyl acrylate, methacrylic-acid hydroxymethyl, methacrylic-acid-2-hydroxyethyl, 2-hydroxypropyl methacrylate, N-methylol acrylamide, allyl alcohol, etc. are mentioned.

[0041] As a monomer which has a cross-linking functional group, it is listed below.

[0042] The polymerization nature monomer which has a block isocyanate radical can be easily manufactured carrying out the addition reaction of the well-known block agent to the polymerization nature monomer which has isocyanate radicals, such as 2-methacryloiloxy-ethyl isocyanate, or by carrying out the addition reaction of the compound which has an isocyanate radical and a block isocyanate radical to the vinyl system copolymer which has the hydroxyl group and carboxyl group which were mentioned above. The compound which has an isocyanate radical and a block isocyanate radical can be easily obtained by carrying out the addition reaction of as well-known the block agent as a diisocyanate compound at about 1:1 rate by the mole ratio.

[0043] As a monomer which has an epoxy group, the acrylate monomer which has glycidyl (meta) acrylate and an alicyclic epoxy group (meta) is mentioned, for example.

[0044] As a monomer which has a 1 and 3-dioxolane-2-ON-4-IRU radical, 1, 3-dioxolane-2-ON-4-ylmethyl (meta) acrylate, 1, and 3-dioxolane-2-ON-4-ylmethyl vinyl ether etc. is mentioned, for example.

[0045] As a polymerization initiator, \*\*\*\* azo compounds, such as \*\*\*\* peroxide; azobis isobutyl nitril, such as t-butyl peroxybenzoate, G t-butyl peroxide, cumene par hydroxide, acetyl peroxide, benzoyl peroxide, and lauroyl peroxide, azobis-2,4-dimethylvaleronitrile, and azobis cyclohexane carbonitrile, etc. are mentioned, for example.

[0046] With an anionic radical content acrylic monomer, further as a solvent used in case the polymerization of other monomers which may be copolymerized with these monomers if needed is carried out For example, \*\*\*\* aliphatic hydrocarbons, such as a hexane and a mineral spirit; Benzene, \*\*\*\* ester solvents [, such as \*\*\*\* aromatic-hydrocarbons-solvent; butyl acetate ], such as toluene and a xylene; A methyl ethyl ketone, \*\*\*\* ketones, such as isobutyl methyl ketone; A methanol, ethanol, \*\*\*\* alcohols solvents, such as a butanol and isopropyl alcohol; \*\*\*\* aprotic polar solvents, such as dimethylformamide, dimethyl sulfoxide, N-methyl pyrrolidone, and a pyridine, etc. are mentioned. These solvents can also use together and use two or more sorts.

[0047] The anionic microencapsulation pigment content aquosity dispersion liquid by the phase inversion method are the following, and are made and manufactured.

[0048] The anionic organic high molecular compounds which have self-dispersion power or dissolution ability to water in a phase inversion method, an organic pigment, or a mixture with carbon black (a composite or complex), Or although anything can be used as long as especially the organic solvent used in case a mixture with an organic pigment or carbon black, a curing agent, and an anionic organic high molecular compound is made into an organic solvent phase is not limited and may dissolve anionic organic high molecular compounds The alcohols solvent like the acetone from the field of the ease of the solvent removal at the time of manufacture, the ester solvent; ethanol like the ketones; ethyl acetate like a methyl ethyl ketone, and isopropyl alcohol; the solvent of the low-boiling point of the aromatic hydrocarbons solvent like benzene etc. is desirable.

[0049] The rate of anionic organic high molecular compounds has the desirable range of the 25 - 186 weight section to the 100 weight sections of an organic pigment or carbon black, and especially its range of the 30 - 150 weight section is desirable.

[0050] Although I hear that the cross linking agent and the high molecular compound are dissolving into anionic organic high molecular compounds and it has them that it is especially desirable for the mixture (a composite or complex) which is an organic phase, without a pigment condensing in any way minutely

in organic high molecular compounds at homogeneity while distributed stabilization is carried out, it is never limited only to this.

[0051] Although not limited, if it limits especially as a distributed stabilization process of this mixture for illustrating only what [ those ] are especially typical also by striking (1) A powder organic pigment or carbon black is made to micro-disperse-ize in anionic organic high molecular compounds using various dispersers, such as a bead mill, a roll mill, and a sand mill. Subsequently The approach that a curing agent, a high molecular compound, etc. are said that you make it dissolve or decentralize, Or the sentiment cake after composition of (2) organic pigments or the wet cake of carbon black, The thing of a condition [ having made water decentralize a pigment freely ] is made to micro-disperse-ize by used and carrying out Flushing of the various dispersers, such as a kneader, into the anionic organic high molecular compounds before neutralization. Namely, subsequently The approach that a curing agent, a high molecular compound, etc. are said that you make it dissolve or decentralize etc. is mentioned. In these distributed approaches, in order to obtain an ultrafine particle, bead mill distribution or the approach of carrying out Flushing is more desirable.

[0052] Moreover, since a sentiment cake is used, the desiccation process of organic pigments is not needed, it becomes energy saving and the firm condensation which takes place into a desiccation process moreover does not take place at all, either, the usefulness of especially the latter approach is very high.

[0053] Furthermore, the pigment derivative which has a dialkyl aminomethyl radical, a SUFONSAN radical, a SUFON amide group, a phthalimide radical, etc. for the purpose of distributed stabilization; pigment agents, such as the "Sol Spurs 24000" etc. by "BYK-160" made from big KEMI, "BYK-166", and Zeneka Co., etc. can be used, and distributed time amount etc. can also be shortened.

[0054] in order to make self-distribution (phase inversion emulsification) easy, and in order to make solvent removal actuation simple -- mixing -- as for the amount of the solvent used in the living body, stopping as low as possible is desirable, and, as for the viscosity of such a field to these mixtures, preparing to 10000 or less CPs is desirable.

[0055] Although self-distribution (phase inversion emulsification) is carried out throwing water into the organic phase of a mixture, or by supplying this organic phase underwater, as the approach, the microencapsulation pigment made into the purpose can be formed by supplying another side slowly into it in an instant, agitating either an organic phase or water moderately.

[0056] Since a class, a rate, etc. of an agitator in such churning seldom affect the magnitude of the particle formed, especially the class or agitating speed of an agitator are not restricted.

[0057] In such a process, although it is possible for the thing of the above-mentioned procedure to also make a sufficiently detailed microencapsulation pigment, as an approach of making a still more detailed thing, it is carrying out phase inversion emulsification, hitting a supersonic wave to an organic phase. Although especially the frequency of the supersonic wave is not limited, it is 10-200kHz preferably.

[0058] In case the so-called neutralization type of anionic organic high molecular compounds are used, only an initial complement needs to make the bases for neutralization dissolve in an organic phase or the aqueous phase beforehand. It is more desirable to dissolve bases in the aqueous phase in consideration of condensation of the pigment in an organic phase especially.

[0059] Moreover, even if the cross linking agent used in order to carry out gelation processing of the formed capsule wall, or in order to raise the film reinforcement after film formation of recording ink is the case where the compound of \*\*\*\* water solubility of for example, polyamine is used, it needs to dissolve only an initial complement in an organic phase beforehand.

[0060] According to the gestalt with which practical use is presented, the anionic microencapsulation pigment content aquosity dispersion liquid obtained by these various approaches can also be used as it is, or they can perform desolventization and it can also be used for them as an aquosity dispersing element.

[0061] General distillation, a vacuum distillation method, etc. are mentioned as an approach of performing desolventization.

[0062] The method (the \*\*\*\* method) of obtaining anionic microencapsulation pigment content aqueous dispersion liquid is based on the following procedures by, using the same ingredient as the above on the other hand, and neutralizing all the anionic all [ a part or ] for the water cake which consists of anionic radical content organic high molecular compounds and an organic pigment, or carbon black using a basic compound.

(1) Distribute anionic organic high molecular compounds and a pigment in an alkaline aqueous medium. Moreover, it heat-treats if needed and gelation of resin is attained.

(2) By making pH into neutrality or acidity, carry out hydrophobing of the resin and fix resin to a pigment strongly.

(4) Perform filtration and rinsing if needed.

(5) Neutralize a carboxyl group as a basic compound is also, and re-distribute in an aqueous medium. Moreover, it heat-treats if needed and gelation of resin is attained.

[0063] As an approach of distributing the anionic organic high molecular compounds and pigment in a process (1) in an alkaline aqueous medium, the two following approaches are suitable.

(1) Distribute in an aqueous medium after kneading a pigment in an organic solvent medium.

(2) Mix or knead a pigment in an aqueous medium.

[0064] By the approach of \*\*\*\*\* (1), a pigment and the organic solvent solution of anionic organic high molecular compounds are first distributed minutely using well-known dispersers, such as a ball mill, a sand mill, and a colloid mill.

[0065] Although all the things for which the organic solvent used is generally used at this time can be used, the solubility over resin is good, the thing and vapor pressure in which the composition top of resin does not have a problem, either are higher than water, and what is easy to carry out desolventization, and a thing with water and a miscibility are still more desirable. As such a solvent, an acetone, a methyl ethyl ketone, a methanol, ethanol, n-propanol, isopropanol, ethyl acetate, a tetrahydrofuran, etc. are mentioned, for example. Although the miscibility with water is low, methyl isopropyl ketone, a methyl-n-propyl ketone, isopropyl acetate, n-propyl acetate, a methylene chloride, benzene, etc. can be used for this approach.

[0066] In order to distribute the dispersing element which consists of the pigment and anionic organic high molecular compounds which were distributed in the organic solvent medium in an aqueous medium

(1) The approach which neutralizes the carboxyl group of anionic organic high molecular compounds using a basic compound, hydrophilic-property-izes anionic organic high molecular compounds, and water is made to distribute, Or the method of making water distribute the dispersing element which consists of the anionic organic high molecular compounds and pigment which were neutralized using (2) basicity compounds is mentioned.

[0067] As the distributed approach to water, the following approaches are suitable.

(a) Water is dropped after neutralizing the dispersing element which consists of anionic organic high molecular compounds and a pigment using a basic compound.

(b) Water is dropped at the dispersing element which consists of the anionic organic high molecular compounds and pigment which were neutralized using the basic compound.

(c) The water containing a basic compound is dropped at the dispersing element which consists of anionic organic high molecular compounds and a pigment.

(d) Neutralize that a basic compound is also about the dispersing element which consists of anionic organic high molecular compounds and a pigment, and add in a water medium.

(e) Add the dispersing element which consists of the anionic organic high molecular compounds and pigment which were neutralized using the basic compound in an aqueous medium.

(f) Add the dispersing element which consists of anionic organic high molecular compounds and a

pigment in the water medium containing a basic compound.

[0068] When distributing in water, you may carry out using high SHIEA churning with churning by usual low SHIEA, a homogenizer, etc., or a supersonic wave. Moreover, a surfactant, protective colloid, etc. can also be used together in the range in which the water resisting property of a paint film is not remarkably reduced as the purpose which assists the distribution to an aqueous medium is also.

[0069] As a basic compound, a sodium hydroxide, a potassium hydroxide, the alkali-metal; ammonia like a lithium hydroxide, triethylamine, tributylamine, dimethylethanolamine, diisopropanolamine, the organic amine like a morpholine, etc. are mentioned, for example.

[0070] It neutralizes first using the basic compound which described above the carboxyl group of anionic organic high molecular compounds, and the approach of kneading resin and a pigment in the aqueous medium which is the approach of \*\* (2) which can apply anionic organic high molecular compounds and a pigment to the \*\* (1) process distributed in an alkaline aqueous medium is mixed or kneaded with a pigment in an aqueous medium. At this time, even if the resin dissolved or distributed in water contains the organic solvent, it may not interfere, it may perform desolventization, and may be the medium of only water substantially. Both a powdered pigment an aqueous slurry and a filter press cake can be used for a pigment. When distributing in an aqueous medium, in order to simplify a production process, as for a pigment, it is desirable to use few aqueous slurries or filter press cakes of secondary condensation of a pigment particle. The same approach as the case of distribution in an organic solvent medium and the same ingredient of the kneading approach, an organic solvent, and a basic compound are usable.

[0071] an organic solvent system and an aqueous system -- even if it is the case of which kneading, a pigment agent and a wetting agent can also be used in the range in which the water resisting property of a record image is not reduced for the purpose which assists distribution of a pigment.

[0072] Moreover, before \*\*\*\*(ing) by being after kneading in case a pigment is kneaded or, the curing catalyst of matter other than a pigment, for example, a color, an anti-oxidant, an ultraviolet ray absorbent, and a coating binder, a rust-proofer, perfume, drugs, etc. can also be added.

[0073] the operating rate of anionic organic high molecular compounds -- the 100 weight sections of an organic pigment -- receiving -- the 25 - 186 weight section -- desirable -- 30 to 150 weight -- the section -- within the limits is suitable. Since it is in the inclination whose allowances on the design of mix are lost when there are few operating rates of anionic organic high molecular compounds than 25 weight sections, it was in the inclination which stops being able to distribute a pigment easily sufficiently minutely, and the rate of the pigment in a dispersing element decreases when [ than the 186 weight sections ] more and a watercolor pigment dispersing element is used for recording ink, it is not desirable.

[0074] Furthermore, when attaining gelation of anionic organic high molecular compounds by heat-treatment after kneading a pigment, it is desirable to perform the nonvolatile matter of the dispersion liquid after kneading at 10% or less preferably 15% or less.

[0075] Moreover, although it will be satisfactory in any way if whenever [ stoving temperature ] is beyond temperature to which bridge formation of resin progresses, a desirable temperature requirement is 70 degrees C - 200 degrees C. Since whenever [ stoving temperature ] is in the inclination which crystal growth is carried out depending on the class of pigment, or distributed stability breaks, and is hard to encapsulate when bridge formation time amount is taken too much and whenever [ stoving temperature ] exceeds 200 degrees C at less than 70 degrees C, it is not desirable.

[0076] \*\*\*\* performed in order to fixing-ize resin strongly to the pigment by which micro-disperse was carried out into the aqueous medium hydrophobicity-izes resin by adding an acid compound for the carboxyl group of the anionic organic high molecular compounds neutralized with the basic compound, and making pH into neutrality or acidity.

[0077] As an acid compound used, although the organic acids like a hydrochloric acid, a sulfuric acid, phosphoric acid, the inorganic-acids; formic acid like a nitric acid, an acetic acid, and a propionic acid can be used for example, the hydrochloric acid or sulfuric acid also with the large \*\*\*\* effectiveness with

little [ and ] organic substance is desirable. [ under wastewater ] Although pH at the time of \*\*\*\* has the desirable range of 2-6, there are some which are decomposed with an acid depending on a pigment, and, in the case of such a pigment, it is desirable to \*\*\*\* in the range of pH 4-7. Before performing \*\*\*\*, it is desirable to remove beforehand the organic solvent which exists in a system using approaches, such as vacuum distillation.

[0078] Filtration and rinsing are performed after \*\*\*\* if needed, and the water cake of a distributed pigment is obtained. As the filtration approach, well-known approaches, such as suction filtration, pressure filtration, and centrifugal separation, are employable.

[0079] This water cake is re-distributed in an aqueous medium, holding a detailed condition without a pigment particle condensing by re-neutralizing a carboxyl group, without making it dry, as a basic compound is also with the condition of having carried out water. Concomitant use with independence, such as an organic amine compound which can volatilize [ diethanolamine / alkali metal, such as a sodium hydroxide, a potassium hydroxide, and a lithium hydroxide, nor / neither / triethanolamine, diethanolamine ] easily in consideration of redispersible and the water resisting property of recording ink as a basic compound, or these, and the volatile amine compound like ammonia, triethylamine, and dimethylethanolamine is desirable.

[0080] Thus, without the so-called auxiliary materials, such as an emulsifier, capsulation of a minute particle is possible also for \*\*, and the anionic microencapsulation pigment used by this invention can be made very simple, and can prepare a minute capsule in any way.

[0081] The actual measurement which added and averaged the major axis and minor axis of a pigment of dozens samples is used for the mean particle diameter of the organic pigment in the microencapsulation pigment used by this invention using the photograph taken with the electron microscope.

[0082] The mean particle diameter of the microencapsulation pigment used by this invention can also be measured using the particle diameter measuring device of a laser-doppler method, although it is desirable to use the actual measurement measured with the electron microscope since a some difference comes out with a particle diameter measuring method.

[0083] Thus, the distributed stability of a pigment is improved more than before, and the anionic microencapsulation pigment content aqueous dispersion liquid obtained have the advantage that engine performance, such as definition of recording ink, lightfastness, color rendering properties, and transparency, improves, by using it as a color material of recording ink. Moreover, since the pigment concentration in a microcapsule is high, versatility is high, and since labor-saving of the process which distributes a pigment can be performed, there is also an advantage that labor-saving of distributed energy and an effort can be attained. Moreover, in order not to use a surfactant etc., a water resisting property also improves. Furthermore, since the oily curing agent and the oily vehicle for recording ink which were not able to be used conventionally can be included in the capsule of a microencapsulation pigment, the width of face of the ingredient which can be used can also manufacture breadth and direct recording ink.

[0084] As claim 1 prescribed, the content of the organic pigment in an anionic microencapsulation pigment has 35 - 80% of the weight of the desirable range. Since the resin concentration in a capsule becomes high when there is less content of the organic pigment in an anionic microencapsulation pigment than 35% Since versatility is missing since an additive and compatibility, such as resin for recording ink, and a solvent, an assistant, may be restricted or the addition of the additive etc. is restricted, and the pigment concentration in a capsule becomes low further, As a result of making high the operating rate of the microencapsulation pigment in recording ink in order not to raise the depth of shade or to raise the depth of shade when it is used as aqueous dispersion liquid as recording ink, since it is in the inclination for the viscosity of recording ink to become high, it is not desirable. Moreover, when there is more content of the organic pigment in an anionic microencapsulation pigment than 80 % of the

weight, since it is in the inclination which stops being able to distribute an organic pigment easily minutely, it is not desirable.

[0085] Moreover, since blinding of the nozzle of a jet ink printer is carried out when the maximum particle diameter of an anionic microencapsulation pigment becomes larger than 1000nm, as claim 2 prescribed, the maximum particle diameter of an anionic microencapsulation pigment is 1000nm or less, and what is 500nm or less is more desirable [ the particle diameter ].

[0086] Furthermore, the mean particle diameter of the organic pigment in the anionic microencapsulation pigment has desirable 300nm or less, and especially its 250nm or less is desirable. the case where it is used as recording ink since it will sediment, or it will be encapsulated after the pigment has condensed on the occasion of microencapsulation when the microencapsulation pigment in dispersion liquid saves at a long period of time if the mean particle diameter of the organic pigment to be used becomes larger than 300nm -- color enhancement -- transparent -- it is -- when definition is inferior and you record on an OHP sheet etc. especially, transparency of light interrupts and a beautiful color projects -- since it is in the inclination which is not, it is not desirable .

[0087] As for the anionic organic high molecular compounds in the anionic microencapsulation pigment of this invention, it is desirable to be used in the form of the salt of alkali metal or an organic amine. Although it is in the inclination for the water resisting property of the record image to worsen since an inorganic base remains in a record image when it is used in the form of the salt of alkali metal, such as a sodium hydroxide, a potassium hydroxide, and a lithium hydroxide, it is desirable from excelling in redispersible and the dependability of recording ink becoming high.

[0088] As the above-mentioned organic amine, organic amines of a high-boiling point which cannot volatilize easily, such as ammonia, triethylamine, tributylamine, dimethylethanolamine, diisopropanolamine, volatile amine compound; diethanolamine like a morpholine, and triethanolamine, are mentioned, for example.

[0089] Below 70 weight sections of the content of the anionic microencapsulation pigment contained in the anionic microencapsulation pigment content aqueous dispersion liquid for recording ink of this invention are desirable in the aqueous dispersion-liquid 100 weight section, its range of 2 - 60 weight section is more desirable to it, and especially its range of 10 - 50 weight section is desirable to it. Since condensation of a microcapsule takes place since it is in the inclination for aqueous dispersion liquid to present the shape of a solid substantially when the content of the microencapsulation pigment in aqueous dispersion liquid becomes higher than 70 weight sections, and distribution is needed again, it is not desirable. moreover, when the content of the microencapsulation pigment in aqueous dispersion liquid became less than 2 weight sections and it is used for recording ink, since it is in the inclination which does not profit have the enough depth of shade, it is not desirable. Considering adding the additive for raising the engine performance to recording ink, when there are few contents of the microencapsulation pigment in aqueous dispersion liquid than 10 weight sections, since it is in the inclination for the addition of an additive to be restricted, it is not desirable.

[0090] The recording ink containing the aqueous dispersion liquid containing the anionic microencapsulation pigment of this invention mixes the anionic microencapsulation pigment content aqueous dispersion liquid and the water-soluble organic solvent which were explained above, water, etc., and is prepared. Furthermore, water soluble resin, an organic amine, a surfactant, antiseptics, a viscosity controlling agent, pH regulator, a chelating agent, etc. can also be added if needed.

[0091] When the saturation of the depth of shade as recording ink, definition, transparency, and a hue etc. is taken into consideration, the content rate of the anionic microencapsulation pigment content aqueous dispersion liquid in the recording ink of this invention has 1 - 100% of the weight of the desirable range, and 5 - 100% of the weight of especially its range is desirable. Considering offering recording ink directly especially, it cannot be overemphasized that 100 % of the weight is desirable.

[0092] As a water-soluble organic solvent used for recording ink, for example Methyl alcohol, Ethyl



alcohol, n-butyl alcohol, isobutyl alcohol, Alcohols, such as tert-butyl alcohol, n-propyl alcohol, and isopropyl alcohol; Dimethyl formaldehyde, Amides, such as dimethylacetamide; Ketones; tetrahydrofurans, such as an acetone and a methyl ethyl ketone, Dioxane, ethylene glycol methyl ether, ethylene glycol ethyl ether, Diethylene-glycol methyl ether, diethylene-glycol ethyl ether, Ether, such as the triethylene glycol monomethyl ether and TORIECHIREN ethylene glycol monoethyl ether, Ethylene glycol, Propylene glycol, a butylene glycol, triethylene glycol, Polyhydric-alcohol; N-methyl-pyrrolidones, such as 1, 2, 6-hexane triol, thiodiglycol, a diethylene glycol, a polyethylene glycol, a polypropylene glycol, and a glycerol, 1,3-dimethyl-2-imidazolidinone, etc. are mentioned. Also in these water-soluble organic solvents, polyhydric alcohol and ether are desirable.

[0093] The content rate of the water-soluble organic solvent in recording ink has 95 or less desirable % of the weight, and 0 - 80% of the weight of especially its range is desirable.

[0094] As water soluble resin used for recording ink if needed, synthetic macromolecules, such as natural protein, such as glue, gelatin, casein, albumin, gum arabic, and fish GURYU, an alginic acid, methyl cellulose, a carboxymethyl cellulose, polyethylene oxide, hydroxyethyl cellulose, polyvinyl alcohol, polyacrylamide, aromatic amide, polyacrylic acid, polyvinyl ether, a polyvinyl pyrrolidone, an acrylic, and polyester, etc. are mentioned, for example.

[0095] Water soluble resin is the purpose which mentions fixable, and quick-drying [ viscosity accommodation and quick-drying ], the content rate of the water soluble resin in the recording ink in the case of being used if needed and using it for recording ink has 30 or less desirable % of the weight, and especially its 20 or less % of the weight is desirable.

[0096] As an organic amine used for recording ink if needed, ethanolamine, diethanolamine, triethanolamine, N-methylethanol amine, N-ethyl diethanolamine, 2-amino-2-methyl propanol, 2-ethyl-2-amino-1,3-propanediol, 2-(aminoethyl) ethanolamine, tris (hydroxymethyl) aminomethane, ammonia, a piperidine, morpholine, etc. are mentioned, for example.

[0097] The manufacture approach of the recording ink of this invention does not need at all a disperser which distributes a pigment, but it is easy agitators, such as DISUPA, and, but only the actuation which carries out churning mixing can manufacture anionic microencapsulation pigment content aqueous dispersion liquid, a water-soluble organic solvent, water, water soluble resin, etc. Moreover, a surfactant, antiseptics, a viscosity controlling agent, pH regulator, a chelating agent, etc. are added and manufactured if needed at the time of churning.

[0098] thus, the manufactured recording ink -- \*\*\*\* for image recording, such as a jet printer, -- it excels in redispersible [ of a record image / the definition the color enhancement, the transparency, the water resisting property or redispersible ] by things, and sharp reduction of the manufacturing cost of recording ink can be aimed at by laborsaving of a distributed process.

[0099]

[Example] Hereafter, this invention is further explained to a detail using an example and the example of a comparison. Below, especially the "section" and "%", as long as there is no notice, the "weight section" and "% of the weight" are expressed.

[0100] <The synthetic example 1> (composition of anionic radical content organic high molecular compounds)

The mixed liquor which consists of the n-butyl methacrylate 175 section, the n-butyl acrylate 10.7 section, the beta-hydroxyethyl methacrylate 37.5 section, the methacrylic-acid 26.8 section, and the "par butyl O" (tert-butylperoxy octoate by Nippon Oil & Fats Co., Ltd.) 5.0 section was prepared.

[0101] Next, after carrying out a temperature up to 75 degrees C, agitating under a N2 seal after teaching the methyl-ethyl-ketone 250 section to a flask, the above-mentioned mixed liquor was dropped for 2 hours, it was made to react at this temperature further for 15 hours, and the acid number of solid content obtained the solution of 70 and the vinyl system resin of number average molecular weight 12500. The nonvolatile matter of this resin solution was 48%. Hereafter, this is written as a resin solution

(A-1).

[0102] <The synthetic example 2> (composition of anionic radical content organic high molecular compounds)

The mixed liquor which consists of the styrene 43 section, the n-butyl acrylate 87.5 section, the beta-hydroxyethyl methacrylate 37.5 section, the methacrylic-acid 19.5 section, and the "par butyl O"5.0 section was prepared.

[0103] Next, after carrying out a temperature up to 75 degrees C, agitating under a N2 seal after teaching the methyl-ethyl-ketone 250 section to a flask, the above-mentioned mixed liquor was dropped for 2 hours, it was made to react at this temperature further for 15 hours, and the acid number of solid content obtained the solution of 48 and the vinyl system resin of number average molecular weight 14000. The nonvolatile matter of this resin solution was 49%. Hereafter, this is written as a resin solution

(A-2).

[0104] <The synthetic example 3> (composition of anionic radical content organic high molecular compounds)

The mixed liquor which consists of the styrene 100 section, the n-butyl acrylate 40.3 section, the beta-hydroxyethyl methacrylate 37.5 section, the methacrylic-acid 9.7 section, and the "par butyl O"5.0 section was prepared.

[0105] Next, after carrying out a temperature up to 75 degrees C, agitating under a N2 seal after teaching the methyl-ethyl-ketone 250 section to a flask, the above-mentioned mixed liquor was dropped for 2 hours, it was made to react at this temperature further for 15 hours, and the acid number of solid content obtained the solution of 24 and the vinyl system resin of number average molecular weight 15000. The nonvolatile matter of this resin solution was 49%. Hereafter, this is written as a resin solution

(A-3).

[0106] <The synthetic example 4> (composition of anionic radical content organic high molecular compounds)

The mixed liquor which consists of the n-butyl methacrylate 175 section, the n-butyl acrylate 10.7 section, the beta-hydroxyethyl methacrylate 37.5 section, the methacrylic-acid 26.8 section, and the "par butyl O"20.0 section was prepared.

[0107] Next, after carrying out a temperature up to 75 degrees C, agitating under a N2 seal after teaching the methyl-ethyl-ketone 250 section to a flask, the above-mentioned mixed liquor was dropped for 2 hours, it was made to react at this temperature further for 15 hours, and the acid number of solid content obtained the solution of 68 and the vinyl system resin of number average molecular weight 5600. The nonvolatile matter of this resin solution was 50%. Hereafter, this is written as a resin solution (A-4).

[0108] <The synthetic example 5> (composition of anionic radical content organic high molecular compounds)

The mixed liquor which consists of the n-butyl methacrylate 153.8 section, the n-butyl acrylate 20.4 section, the beta-hydroxyethyl methacrylate 37.5 section, the methacrylic-acid 38.3 section, and the "par butyl O"5.0 section was prepared. Next, it is [0109] under the N2 seal after teaching the methyl-ethyl-ketone 250 section to a flask. After carrying out a temperature up to 75 degrees C, agitating, the above-mentioned mixed liquor was dropped for 2 hours, it was made to react at this temperature further for 15 hours, and the acid number of solid content obtained the solution of 98 and the vinyl system resin of number average molecular weight 12500. The nonvolatile matter of this resin solution was 51%. Hereafter, this is written as a resin solution (A-5).

[0110] <The synthetic example 6> (composition of anionic radical content organic high molecular compounds)

The mixed liquor which consists of the n-butyl methacrylate 171.4 section, the n-butyl acrylate 6.3 section, the beta-hydroxyethyl methacrylate 37.5 section, the acrylic-acid 34.8 section, and the "par butyl O"20.0 section was prepared.

[0111] Next, after carrying out a temperature up to 75 degrees C, agitating under a N2 seal after teaching the methyl-ethyl-ketone 250 section to a flask, the above-mentioned mixed liquor was dropped for 2 hours, it was made to react at this temperature further for 15 hours, and the acid number of solid content obtained the solution of 95 and the vinyl system resin of number average molecular weight 8800. The nonvolatile matter of this resin solution was 50%. Hereafter, this is written as a resin solution (A-6).  
 [0112] <The synthetic example 7> (for synthetic - gelation processing of anionic radical content organic high molecular compounds)

The mixed liquor which consists of the n-butyl methacrylate 83.8 section, the n-butyl acrylate 89.4 section, the beta-hydroxyethyl methacrylate 37.5 section, the methacrylic-acid 26.7 section, the glycidyl methacrylate 12.5 section, and the "par butyl O"20.0 section was prepared.

[0113] Next, after carrying out a temperature up to 75 degrees C, agitating under a N2 seal after teaching the methyl-ethyl-ketone 250 section to a flask, the above-mentioned mixed liquor was dropped for 2 hours, it was made to react at this temperature further for 15 hours, and the acid number of solid content obtained the solution of 69 and the vinyl system resin of number average molecular weight 10400. The nonvolatile matter of this resin solution was 50%. Hereafter, this is written as a resin solution (A-7).

[0114]

[Table 1]

	樹脂溶液	分子量	酸価	不揮発分%
合成例 1	A-1	1 2 5 0 0	7 0	4 8
合成例 2	A-2	1 4 0 0 0	4 8	4 9
合成例 3	A-3	1 5 0 0 0	2 4	4 9
合成例 4	A-4	5 6 0 0	6 8	5 0
合成例 5	A-5	1 2 5 0 0	9 8	5 1
合成例 6	A-6	8 8 0 0	9 5	5 0
合成例 7	A-7	1 0 4 0 0	6 9	5 0

[0115] <The example 1 of manufacture> (manufacture of the anionic microencapsulation pigment content aqueous dispersion liquid of a copper copper phthalocyanine blue)

The resin solution (A-5) 22.1 section, "fast gene blue, TGR" (the C.I. pigment blue 15 by Dainippon Ink & Chemicals, Inc., and the mean particle diameter of 50nm) which were obtained in the synthetic example 5 As the maximum particle diameter 14.25 sections of 100nm, and a distributed assistant, the dimethyl aminomethyl copper-phthalocyanine 0.75 section, The methyl-ethyl-ketone 78.2 section, "super BEKKAMIN the L-109-60"(melamine resin by Dainippon Ink & Chemicals, Inc.) 4.7 section, and the ceramic bead 300 section After putting into the container made from stainless steel, the mixture was distributed using the bead mill disperser, and the paste for microencapsulation pigments was prepared.

[0116] Next, irradiating a 45kHz supersonic wave at an organic phase, it was dropped into the organic phase, having applied [ ion-exchange-water 50 ] it for 12 minutes, self-distribution (phase inversion emulsification) was performed, and anionic microencapsulation pigment content aqueous dispersion liquid were obtained [ after mixing using an agitator after putting the paste 40.0 above-mentioned section for microencapsulation pigments, and the dimethylamino ethanol 0.4 section into Pori Kapp, and

considering as an organic phase, while agitating this organic phase, and ].

[0117] Furthermore, after making a solvent distill off by distilling these microencapsulation pigment content aqueous dispersion liquid at 85 degrees C, it held at this temperature for 5 hours, and gelation processing of a capsule wall was performed.

[0118] Thus, as a result of measuring the particle size of the microencapsulation pigment in the obtained anionic microencapsulation pigment content aqueous dispersion liquid (MC-1) using "UPA-150" (laser-doppler method particle-size-distribution measurement machine by Nikkiso Co., Ltd.), the volume mean particle diameter of a microencapsulation pigment was 148nm, and the particle 1000nm or more of the maximum particle diameter was 0%. Moreover, the nonvolatile matter concentration of microencapsulation pigment content aqueous dispersion liquid was 24.5%, and the content of the pigment in a microcapsule was 51.7%.

[0119] <The example 2 of manufacture> (manufacture of the anionic microencapsulation pigment content aqueous dispersion liquid of a copper copper phthalocyanine blue)

(1) After adding zirconia-beads 250g whose mean particle diameter is 0.5mm after adding the resin solution (A-4) 15.0 section, the dimethylethanolamine 0.8 section, and the "fast gene blue and TGR"15 section which were obtained in the synthetic example 4 to a glass bottle with a pigment kneading process capacity of 250ml, adding ion exchange water and making it a total amount become the 75 sections, kneading was performed for 4 hours using the paint shaker. The glass bead was carried out the \*\* exception after kneading termination, and what distributed in water the resin which has the carboxyl group neutralized by the base, and the dispersing element which consists of a pigment was obtained.

[0120] (2) Agitating by DISUPA, after adding water to what distributed in water the resin which has the carboxyl group neutralized by the \*\*\*\* base, and the dispersing element which consists of a pigment and diluting twice, it added until resin insolubilized 1 convention hydrochloric acid and it fixed to the pigment. pH at this time was 3-5.

[0121] (3) The salt was rinsed and the water cake was obtained, after carrying out suction filtration of the aqueous medium containing the pigment which filtration and rinsing resin fixed.

[0122] (4) Agitating neutralization and the re-distribution water cake to an aqueous medium using DISUPA, 10% water solution of dimethylethanolamine was added until pH of a dispersing element was set to 8.5-9.5. Furthermore, after continuing churning for 1 hour, water was added, and it adjusted so that a nonvolatile matter might become 20%, and anionic microencapsulation pigment content aqueous dispersion liquid (MC-2) were obtained.

[0123] As a result of measuring the particle size of the microencapsulation pigment in anionic microencapsulation pigment content aqueous dispersion liquid (MC-2) like the example 1 of manufacture, the volume mean particle diameter of a microencapsulation pigment was 170nm, and the particle 1000nm or more was 0%. Moreover, the content of the pigment in a microcapsule was 67%.

[0124] <The example 3 of manufacture> (manufacture of the anionic microencapsulation pigment content aqueous dispersion liquid of the copper copper phthalocyanine blue by mineral salt)

(1) What distributed in water the resin which has the carboxyl group neutralized by the base like the example 2 of pigment kneading process manufacture, and the dispersing element which consists of a pigment was obtained.

[0125] (2) Agitating by DISUPA, after adding water to what distributed in water the resin which has the carboxyl group neutralized by the \*\*\*\* base, and the dispersing element which consists of a pigment and diluting twice, it added until resin insolubilized 1 convention hydrochloric acid and it fixed to the pigment. pH at this time was 3-5.

[0126] (3) The salt was rinsed and the water cake was obtained, after carrying out suction filtration of the aqueous medium containing the pigment which filtration and rinsing resin fixed.

[0127] (4) Agitating neutralization and the re-distribution water cake to an aqueous medium using

DISUPA, the sodium-hydroxide water solution was added 10% until pH of a dispersing element was set to 8.5-9.5. Furthermore, after continuing churning for 1 hour, water was added, and it adjusted so that a nonvolatile matter might become 20%, and anionic microencapsulation pigment content aqueous dispersion liquid (MC-3) were obtained.

[0128] As a result of measuring the particle size of the microencapsulation pigment in anionic microencapsulation pigment content aqueous dispersion liquid (MC-3) like the example 1 of manufacture, the volume mean particle diameter of a microencapsulation pigment was 182nm, and the particle 1000nm or more was 0%. Moreover, the content of the pigment in a microcapsule was 67%.

[0129] <The example 4 of manufacture> (manufacture of the anionic microencapsulation pigment content aqueous dispersion liquid of a copper copper phthalocyanine blue)

Except having used what neutralized the resin which has a carboxyl group in the resin solution (A-2) obtained in the synthetic example 2 100% using dimethylethanolamine, like the example 2 of manufacture, pigment kneading, \*\*\*\*, filtration and rinsing, neutralization, and re-distribution were performed, and the nonvolatile matter obtained 20% of anionic microencapsulation pigment content aqueous dispersion liquid (MC-4).

[0130] As a result of measuring the particle size of the microencapsulation pigment in anionic microencapsulation pigment content aqueous dispersion liquid (MC-4) like the example 2 of manufacture, the volume mean particle diameter of a microencapsulation pigment was 218nm, and the particle 1000nm or more was 0%. Moreover, the content of the pigment in a microcapsule was 67%.

[0131] <The example 5 of manufacture> (manufacture of the anionic microencapsulation pigment content aqueous dispersion liquid of the copper copper phthalocyanine blue which used the anionic organic high molecular compounds of the acid number 25)

(1) The resin which has a carboxyl group in the resin solution (A-3) obtained in the example 3 of pigment kneading process composition was neutralized 100% using dimethylethanolamine. After adding the methyl ethyl ketone of an amount in which the 7.5 sections and the "fast gene blue and TGR"15 section are added by solid content conversion, and resin dissolves the neutralized resin to a glass bottle with a capacity of 250ml, adding ion exchange water and making it a total amount become the 75 sections, zirconia-beads 250g whose mean particle diameter is 0.5mm was added, and kneading was performed for 4 hours using the paint shaker. The glass bead was carried out the \*\* exception after kneading termination, and what distributed in water the resin which has the carboxyl group neutralized by the base, and the dispersing element which consists of a pigment was obtained.

[0132] (2) Agitating by DISUPA, after adding water to what distributed in water the resin which has the carboxyl group neutralized by the \*\*\*\* base, and the dispersing element which consists of a pigment and diluting twice, it added until resin insolubilized 1 convention hydrochloric acid and it fixed to the pigment. pH at this time was 3-5.

[0133] (3) The salt was rinsed and the water cake was obtained, after carrying out suction filtration of the aqueous medium containing the pigment which filtration and rinsing resin fixed.

[0134] (4) Agitating neutralization and the re-distribution water cake to an aqueous medium using DISUPA, 10% water solution of dimethylethanolamine was added until pH of a dispersing element was set to 8.5-9.5. Furthermore, after continuing churning for 1 hour, water was added, and it adjusted so that a nonvolatile matter might become 20%, and anionic microencapsulation pigment content aqueous dispersion liquid (MC-5) were obtained.

[0135] As a result of measuring the particle size of the microencapsulation pigment in anionic microencapsulation pigment content aqueous dispersion liquid (MC-5) like the example 1 of manufacture, the volume mean particle diameter of a microencapsulation pigment was 650nm, and the particle 1000nm or more was 17%. Moreover, the content of the pigment in a microcapsule was 67%.

[0136] <The example 6 of manufacture> (manufacture of the anionic microencapsulation pigment content aqueous dispersion liquid of a Magenta color)

The resin solution (A-1) 23.4 section, "a fast gene super Magenta and RTS" (the C.I. pigment red 122 by Dainippon Ink & Chemicals, Inc., and the mean particle diameter of 45nm) which were obtained in the synthetic example 1 As the maximum particle diameter 14.25 sections of 100nm, and a distributed assistant, the dimethyl aminomethyl Quinacridone 0.75 section, The methyl-ethyl-ketone 76.9 section, "super BEKKAMIN the L-109-60"(melamine resin by Dainippon Ink & Chemicals, Inc.) 4.7 section, and the ceramic bead 300 section After putting into the container made from stainless steel, the mixture was distributed using the bead mill disperser, and the paste for microencapsulation pigments was prepared. [0137] Next, irradiating a 45kHz supersonic wave at an organic phase, it was dropped into the organic phase, having applied [ ion-exchange-water 50 ] it for 12 minutes, self-distribution (phase inversion emulsification) was performed, and anionic microencapsulation pigment content aqueous dispersion liquid were obtained [ after mixing using an agitator after putting the paste 40.0 above-mentioned section for microencapsulation pigments, and the dimethylamino ethanol 0.4 section into Pori Kapp, and considering as an organic phase, while agitating this organic phase, and ].

[0138] Furthermore, after making a solvent distill off by distilling these microencapsulation pigment content aqueous dispersion liquid at 85 degrees C, it held at this temperature for 5 hours, and gelation processing of a capsule wall was performed.

[0139] Thus, as a result of measuring the particle size of the microencapsulation pigment in the obtained anionic microencapsulation pigment content aqueous dispersion liquid (MC-6) like the example 1 of manufacture, the volume mean particle diameter of a microencapsulation pigment was 145nm, and the particle 1000nm or more of the maximum particle diameter was 0%. Moreover, the nonvolatile matter concentration of microencapsulation pigment content aqueous dispersion liquid was 23.2%, and the content of the pigment in a microcapsule was 51.7%.

[0140] <The example 7 of manufacture> (manufacture of the anionic microencapsulation pigment content aqueous dispersion liquid of a Magenta color)

(1) The resin solution (A-4) 15.0 section obtained in the synthetic example 4 to the glass bottle with a pigment kneading process capacity of 250ml, The dimethylethanolamine 0.8 section and "a fast gene super Magenta and RTS" (the C.I. pigment red 122 by Dainippon Ink & Chemicals, Inc., and the mean particle diameter of 45nm) After adding zirconia-beads 250g whose mean particle diameter is 0.5mm after adding the maximum particle diameter 15 sections of 100nm, adding ion exchange water and making it a total amount become the 75 sections, the paint shaker performed kneading for 4 hours. The glass bead was carried out the \*\* exception after kneading termination, and what distributed in water the resin which has the carboxyl group neutralized by the base, and the dispersing element which consists of a pigment was obtained.

[0141] (2) Agitating by DISUPA, after adding water to what distributed in water the resin which has the carboxyl group neutralized by the \*\*\*\* base, and the dispersing element which consists of a pigment and diluting twice, it added until resin insolubilized 1 convention hydrochloric acid and it fixed to the pigment. pH at this time was 3-5.

[0142] (3) The salt was rinsed and the water cake was obtained, after carrying out suction filtration of the aqueous medium containing the pigment which filtration and rinsing resin fixed.

[0143] (4) Agitating neutralization and the re-distribution water cake to an aqueous medium using DISUPA, 10% water solution of dimethylethanolamine was added until pH of a dispersing element was set to 8.5-9.5. Furthermore, after continuing churning for 1 hour, water was added, and it adjusted so that a nonvolatile matter might become 20%, and anionic microencapsulation pigment content aqueous dispersion liquid (MC-7) were obtained.

[0144] As well as the example 1 of manufacture as a result of measuring the particle size of the microencapsulation pigment in anionic microencapsulation pigment content aqueous dispersion liquid (MC-7), the volume mean particle diameter of a microencapsulation pigment was 176nm, and the particle 1000nm or more was 0%. Moreover, the content of the pigment in a microcapsule was 67%.

[0145] <The example 8 of manufacture> (manufacture of the anionic microencapsulation pigment content aqueous dispersion liquid of the Magenta color whose content of an organic pigment is 83%) In the example 7 of manufacture, except having made into the 6.0 sections the amount of the resin solution (A-4) used at a pigment kneading process, pigment kneading, \*\*\*\*, filtration and rinsing, neutralization, and re-distribution were performed like the example 7 of manufacture, and the nonvolatile matter obtained 20% of anionic microencapsulation pigment content aqueous dispersion liquid (MC-8).

[0146] As a result of measuring the particle size of the microencapsulation pigment in anionic microencapsulation pigment content aqueous dispersion liquid (MC-8) like the example 1 of manufacture, the volume mean particle diameter of a microencapsulation pigment was 250nm, and the particle 1000nm or more was 0%. Moreover, the content of the pigment in a microcapsule was 83%.

[0147] <The example 9 of manufacture> (manufacture of the anionic microencapsulation pigment content aqueous dispersion liquid of the Magenta color whose content of an organic pigment is 75%) In the example 7 of manufacture, the amount of the resin solution (A-4) used at a pigment kneading process was made into the 10.0 sections, like the example 7 of manufacture, pigment kneading, \*\*\*\*, filtration and rinsing, neutralization, and re-distribution were performed, and the nonvolatile matter obtained 20% of anionic microencapsulation pigment content aqueous dispersion liquid (MC-9) except having used the ethyl ethyl ketone 5.0 section with the resin solution (A-4).

[0148] As a result of measuring the particle size of the microencapsulation pigment in anionic microencapsulation pigment content aqueous dispersion liquid (MC-9) like the example 1 of manufacture, the volume mean particle diameter of a microencapsulation pigment was 180nm, and the particle 1000nm or more was 0%. Moreover, the content of the pigment in a microcapsule was 75%.

[0149] <The example 10 of manufacture> (manufacture of the anionic microencapsulation pigment content aqueous dispersion liquid of the Magenta color whose content of an organic pigment is 33%) (1) After adding zirconia-beads 250g whose mean particle diameter is 0.5mm after adding the resin solution (A-4) 20.0 section, the dimethylethanolamine 1.1 section, and the fast gene super Magenta and "RTS" 5.0 section which were obtained in the synthetic example 4 to a glass bottle with a pigment-content powder process capacity of 250ml, adding ion exchange water and making it a total amount become the 75 sections, kneading was performed for 4 hours using the paint shaker. The glass bead was carried out the \*\* exception after kneading termination, and what distributed in water the resin which has the carboxyl group neutralized by the base, and the dispersing element which consists of a pigment was obtained.

[0150] Next, like the example 7 of manufacture, \*\*\*\*, filtration and rinsing, neutralization, and re-distribution were performed, and the nonvolatile matter obtained 20% of anionic microencapsulation pigment content aqueous dispersion liquid (MC-10).

[0151] As well as the example 1 of manufacture as a result of measuring the particle size of the microencapsulation pigment in anionic microencapsulation pigment content aqueous dispersion liquid (MC-10), the volume mean particle diameter of a microencapsulation pigment was 224nm, and the particle 1000nm or more was 0%. Moreover, the content of the pigment in a microcapsule was 33%.

[0152] <The example 11 of manufacture> (manufacture of the anionic microencapsulation pigment content aqueous dispersion liquid of the Magenta color which used the organic pigment whose mean particle diameter is 250nm)

It replaces with "a fast gene super Magenta and RTS" in the example 7 of manufacture. Except having used "clo MOFUTARU red and DPP-BO" (the Ciba-Geigy C.I. pigment red 254, mean particle diameter of 250nm, the maximum particle diameter of 400nm) Like the example 7 of manufacture, pigment kneading, \*\*\*\*, filtration and rinsing, neutralization, and re-distribution were performed, and the nonvolatile matter obtained 20% of anionic microencapsulation pigment content aqueous dispersion liquid (MC-11).

[0153] As well as the example 1 of manufacture as a result of measuring the particle size of the



microencapsulation pigment in anionic microencapsulation pigment content aqueous dispersion liquid (MC-11), the volume mean particle diameter of a microencapsulation pigment was 283nm, and the particle 1000nm or more of the maximum particle diameter was 0%. Moreover, the content of the pigment in a microcapsule was 67%.

[0154] <The example 12 of manufacture> (manufacture of the anionic microencapsulation pigment content aqueous dispersion liquid of a yellow color)

The resin solution (A-1) 23.4 section, "SHIMURA fast yellow and 8GTF" (the C.I. pigment yellow 17 by Dainippon Ink & Chemicals, Inc., and the mean particle diameter of 60nm) which were obtained in the synthetic example 1 The maximum particle diameter 15.0 sections of 120nm, the methyl-ethyl-ketone 76.9 section, "super BEKKAMIN the L-109-60"(melamine resin by Dainippon Ink & Chemicals, Inc.) 4.7 section, and the ceramic bead 300 section After putting into the container made from stainless steel, the mixture was distributed using the bead mill disperser, and the paste for microencapsulation pigments was prepared.

[0155] Next, irradiating a 45kHz supersonic wave at an organic phase, it was dropped into the organic phase, having applied [ ion-exchange-water 50 ] it for 12 minutes, self-distribution (phase inversion emulsification) was performed, and anionic microencapsulation pigment content aqueous dispersion liquid were obtained [ after mixing using an agitator after putting the paste 40.0 above-mentioned section for microencapsulation pigments, and the dimethylamino ethanol 0.4 section into Pori Kapp, and considering as an organic phase, while agitating this organic phase, and ].

[0156] Furthermore, after making a solvent distill off by distilling these microencapsulation pigment content aqueous dispersion liquid at 85 degrees C, it held at this temperature for 5 hours, and gelation processing of a capsule wall was performed.

[0157] Thus, as a result of measuring the particle size of the microencapsulation pigment in the obtained anionic microencapsulation pigment content aqueous dispersion liquid (MC-12) like the example 1 of manufacture, the volume mean particle diameter of a microencapsulation pigment was 191nm, and the particle 1000nm or more of the maximum particle diameter was 0%. Moreover, the nonvolatile matter concentration of microencapsulation pigment content aqueous dispersion liquid was 23.8%, and the content of the pigment in a microcapsule was 51.7%.

[0158] <The example 13 of manufacture> (manufacture of the anionic microencapsulation pigment content aqueous dispersion liquid of a yellow color)

(1) After adding zirconia-beads 250g whose mean particle diameter is 0.5mm after adding the resin solution (A-1) 15.6 section, the dimethylethanolamine 0.8 section, and the SHIMURA first yellow and "8GTF" 15 section which were obtained in the synthetic example 1 to a glass bottle with a pigment kneading process capacity of 250ml, adding ion exchange water and making it a total amount become the 75 sections, kneading was performed for 4 hours using the paint shaker. The glass bead was carried out the \*\* exception after kneading termination, and what distributed in water the resin which has the carboxyl group neutralized by the base, and the dispersing element which consists of a pigment was obtained.

[0159] (2) Agitating by DISUPA, after adding water to what distributed in water the resin which has the carboxyl group neutralized by the \*\*\*\* base, and the dispersing element which consists of a pigment and diluting twice, it added until resin insolubilized 1 convention hydrochloric acid and it fixed to the pigment. pH at this time was 3-5.

[0160] (3) The salt was rinsed and the water cake was obtained, after carrying out suction filtration of the aqueous medium containing the pigment which filtration and rinsing resin fixed.

[0161] (4) Agitating neutralization and the re-distribution water cake to an aqueous medium using DISUPA, 10% water solution of dimethylethanolamine was added until pH of a dispersing element was set to 8.5-9.5. Furthermore, after continuing churning for 1 hour, water was added, and it adjusted so that a nonvolatile matter might become 20%, and the anionic microencapsulation pigment content

aquosity dispersion liquid (MC-13) of a yellow color were obtained.

[0162] As well as the example 1 of manufacture as a result of measuring the particle size of the microencapsulation pigment in anionic microencapsulation pigment content aquosity dispersion liquid (MC-13), the volume mean particle diameter of a microencapsulation pigment was 183nm, and the particle 1000nm or more was 0%. Moreover, the content of the pigment in a microcapsule was 67%.

[0163] <The example 14 of manufacture> (manufacture of the anionic microencapsulation pigment content aquosity dispersion liquid of the yellow color which used the organic pigment whose mean particle diameter is 220nm)

It replaces with "SHIMURA fast yellow and 8GTF" in the example 13 of manufacture. It is made to be the same as that of the example 13 of manufacture except having used "SHIMURA fast yellow and 4192" (the C.I. pigment yellow 154 by Dainippon Ink & Chemicals, Inc., mean particle diameter of 220nm, the maximum particle diameter of 350nm). Pigment kneading, \*\*\*\*, filtration and rinsing, neutralization, and re-distribution were performed, and the nonvolatile matter obtained 20% of anionic microencapsulation pigment content aquosity dispersion liquid (MC-14).

[0164] As well as the example 1 of manufacture as a result of measuring the particle size of the microencapsulation pigment in anionic microencapsulation pigment content aquosity dispersion liquid (MC-14), the volume mean particle diameter of a microencapsulation pigment was 245nm, and the particle 1000nm or more was 0%. Moreover, the content of the pigment in a microcapsule was 67%.

[0165] <The example 15 of manufacture> (manufacture of the anionic microencapsulation pigment content aquosity dispersion liquid of the cyanogen color which used the base of a non-volatile)

(1) After adding zirconia-beads 250g whose mean particle diameter is 0.5mm after adding the resin solution (A-6) 15.0 section, the dimethylethanolamine 1.1 section, and the "fast gene blue and TGR" 15 section which were obtained in the synthetic example 6 to a glass bottle with a pigment kneading process capacity of 250ml, adding ion exchange water and making it a total amount become the 75 sections, kneading was performed for 4 hours using the paint shaker. The glass bead was carried out the \*\* exception after kneading termination, and what distributed in water the resin which has the carboxyl group neutralized by the base, and the dispersing element which consists of a pigment was obtained.

[0166] (2) Agitating by DISUPA, after adding water to what distributed in water the resin which has the carboxyl group neutralized by the \*\*\*\* base, and the dispersing element which consists of a pigment and diluting twice, it added until resin insolubilized 1 convention hydrochloric acid and it fixed to the pigment. pH at this time was 3-5.

[0167] (3) The salt was rinsed and the water cake was obtained, after carrying out suction filtration of the aquosity medium containing the pigment which filtration and rinsing resin fixed.

[0168] (4) Agitating neutralization and the re-distribution water cake to an aquosity medium using DISUPA, the sodium-hydroxide water solution was added 10% until pH of a dispersing element was set to 8.5-9.5. Furthermore, after continuing churning for 1 hour, water was added, and it adjusted so that a nonvolatile matter might become 20%, and the anionic microencapsulation pigment content aquosity dispersion liquid (MC-15) of a blue color were obtained.

[0169] As well as the example 1 of manufacture as a result of measuring the particle size of the microencapsulation pigment in anionic microencapsulation pigment content aquosity dispersion liquid (MC-15), the volume mean particle diameter of a microencapsulation pigment was 152nm, and the particle 1000nm or more was 0%. Moreover, the content of the pigment in a microcapsule was 67%.

[0170] <The example 16 of manufacture> (manufacture of the anionic microencapsulation pigment content aquosity dispersion liquid of the Magenta color which used the base of a non-volatile)

It replaces with "fast gene blue and TGR" in the example 15 of manufacture. Except having replaced with 10% sodium-hydroxide water solution further for neutralization, and having used the potassium-hydroxide water solution 10% using "a fast gene super Magenta and RTS" Like the example

15 of manufacture, pigment kneading, \*\*\*\*, filtration and rinsing, neutralization, and re-distribution were performed, and the nonvolatile matter obtained 20% of anionic microencapsulation pigment content aqueous dispersion liquid (MC-16).

[0171] As well as the example 1 of manufacture as a result of measuring the particle size of the microencapsulation pigment in anionic microencapsulation pigment content aqueous dispersion liquid (MC-16), the volume mean particle diameter of a microencapsulation pigment was 178nm, and the particle 1000nm or more was 0%. Moreover, the content of the pigment in a microcapsule was 67%.

[0172] <The example 17 of manufacture> (manufacture of the anionic microencapsulation pigment content aqueous dispersion liquid of the yellow color which used the base of a non-volatile)

In the example 15 of manufacture, it replaced with "fast gene blue and TGR", and using "SHIMURA fast yellow and 8GTF", like the example 15 of manufacture, pigment kneading, \*\*\*\*, filtration and rinsing, neutralization, and re-distribution were performed, and the nonvolatile matter obtained 20% of anionic microencapsulation pigment content aqueous dispersion liquid (MC-17) except having replaced with 10% sodium-hydroxide water solution further for neutralization, and having used the lithium-hydroxide water solution 10%.

[0173] As well as the example 1 of manufacture as a result of measuring the particle size of the microencapsulation pigment in anionic microencapsulation pigment content aqueous dispersion liquid (MC-17), the volume mean particle diameter of a microencapsulation pigment was 182nm, and the particle 1000nm or more was 0%. Moreover, the content of the pigment in a microcapsule was 67%.

[0174] <The example 18 of manufacture> (manufacture of the anionic microencapsulation pigment content aqueous dispersion liquid of the carbon black which carried out gelation processing of a capsule wall)

(1) After adding the zirconia-beads 250 section whose mean particle diameter is 0.5mm after adding the resin solution (A-7) 15.0 section, the dimethylethanolamine 0.8 section, and the "MA-600 (Mitsubishi Chemical middle-class carbon black: mean particle diameter of 18nm)" 15 section which were obtained in the synthetic example 7 to a glass bottle with a pigment kneading process capacity of 250ml, adding ion exchange water and making it a total amount become the 75 sections, kneading was performed for 4 hours using the paint shaker. The glass bead was carried out the \*\* exception after kneading termination, and what distributed in water the resin which has the carboxyl group neutralized by the base, and the dispersing element which consists of a pigment was obtained.

[0175] (2) After adding water to what distributed in water the resin which has the carboxyl group neutralized by the gelation processing base, and the dispersing element which consists of a pigment and diluting 3 times, heating gelation processing was carried out at 120 degrees C in the autoclave.

[0176] (3) It added after carrying out \*\*\*\* gelation processing until resin insolubilized 1 convention hydrochloric acid and it fixed to the pigment in ordinary temperature, agitating by DISUPA. pH at this time was 3-5.

[0177] (4) The salt was rinsed and the water cake was obtained, after carrying out suction filtration of the aqueous medium containing the pigment which filtration and rinsing resin fixed.

[0178] (5) Agitating neutralization and the re-distribution water cake to an aqueous medium using DISUPA, the dimethylamino ethanol water solution was added 10% until pH of a dispersing element was set to 8.5-9.5. Furthermore, after continuing churning for 1 hour, water was added, and it adjusted so that a nonvolatile matter might become 20%, and the anionic microencapsulation pigment content aqueous dispersion liquid (MC-18) of carbon black were obtained.

[0179] As well as the example 1 of manufacture as a result of measuring the particle size of the microencapsulation pigment in anionic microencapsulation pigment content aqueous dispersion liquid (MC-18), the volume mean particle diameter of a microencapsulation pigment was 149nm, and the particle 1000nm or more was 0%. Moreover, the content of the pigment in a microcapsule was 67%.

[0180]

[Table 2]

	樹脂溶液	顔 料	方法	7ミシ	粒子径	N. V.	粗粒	顔料分
製造例 1	A - 5	TGR	転相	DMAE	148nm	24.5%	0%	51.7%
製造例 2	A - 4	TGR	酸析	DMAE	170nm	20%	0%	67%
製造例 3	A - 4	TGR	酸析	NaOH	182nm	20%	0%	67%
製造例 4	A - 2	TGR	酸析	DMAE	218nm	20%	0%	67%
製造例 5	A - 3	TGR	酸析	DMAE	650nm	20%	17%	67%
製造例 6	A - 1	RTS	転相	DMAE	145nm	23.2%	0%	51.7%
製造例 7	A - 4	RTS	酸析	DMAE	176nm	20%	0%	67%
製造例 8	A - 4	RTS	酸析	DMAE	250nm	20%	0%	83%
製造例 9	A - 4	RTS	酸析	DMAE	180nm	20%	0%	75%
製造例10	A - 4	RTS	酸析	DMAE	224nm	20%	0%	33%

[0181]

[Table 3]

	樹脂溶液	顔 料	方法	7ミシ	粒子径	N. V.	粗粒	顔料分
製造例11	A - 4	DPP	酸析	DMAE	283nm	20%	0%	67%
製造例12	A - 1	8GTF	転相	DMAE	191nm	23.8%	0%	51.7%
製造例13	A - 1	8GTF	酸析	DMAE	183nm	20%	0%	67%
製造例14	A - 1	4192	酸析	DMAE	245nm	20%	0%	67%
製造例15	A - 6	TGR	酸析	NaOH	152nm	20%	0%	67%
製造例16	A - 6	RTS	酸析	KOH	178nm	20%	0%	67%
製造例17	A - 6	8GTF	酸析	LiOH	178nm	20%	0%	67%
製造例18	A - 7	C B	酸析	DMAE	149nm	20%	0%	67%

[0182] The cable address in Table 2 and 3 is as follows.

TGR : "fast gene blue and TGR" (C.I. pigment blue 15 by Dainippon Ink &amp; Chemicals, Inc.)

RTS : "a fast gene super Magenta and RTS" (C.I. pigment red 122 by Dainippon Ink &amp; Chemicals, Inc.)

DPP : "clo MOFUTARU red and DPP-BO" (Ciba-Geigy C.I. pigment red 254)

8GTF : "SHIMURA fast yellow and 8GTF" (C.I. pigment yellow 17 by Dainippon Ink &amp; Chemicals, Inc.)

4192: "SHIMURA fast yellow, 4192" (C.I. pigment yellow 154 by Dainippon Ink & Chemicals, Inc.)  
 CB : carbon black DMAE:dimethylamino ethanol particle diameter : Volume mean-particle-diameter N.V.  
 of a microencapsulation pigment: Nonvolatile matter concentration coarse grain : Rate pigment content  
 of a particle with a particle size [ of a microencapsulation pigment ] of 1000nm or more : Content rate of  
 the pigment in a microcapsule [0183] <Example 1> (manufacture of the recording ink which used the  
 microencapsulation pigment dispersion liquid whose pigment content in a microencapsulation pigment is  
 67%)

In the anionic microencapsulation pigment content aqueous dispersion-liquid (MC-2) 37.5 section of the  
 copper phthalocyanine blue obtained in the example 2 of manufacture, the ethylene glycol 7.5 section,  
 the glycerol 5.0 section, the diethylene-glycol monobutyl ether 0.5 section, the  
 ethylene-glycol-monomethyl-ether 15.0 section, the isopropyl alcohol 3.0 section, the diethanolamine 3.0  
 section, and the ion-exchange-water 28.5 section were mixed, and the pigment content prepared the  
 recording ink of 5.0% of cyanogen color in it.

[0184] <Example 2> (manufacture of the recording ink which used the microencapsulation pigment  
 dispersion liquid whose pigment content in a microencapsulation pigment is 67%)

In the example 1, it replaced with the anionic microencapsulation pigment content aqueous dispersion  
 liquid (MC-2) of the copper phthalocyanine blue obtained in the example 2 of manufacture, and the  
 recording ink of a Magenta color was prepared like the example 1 except having used the anionic  
 microencapsulation pigment content aqueous dispersion liquid (MC-7) of the Magenta color obtained in  
 the example 7 of manufacture.

[0185] <Example 3> (manufacture of the recording ink which used the microencapsulation pigment  
 dispersion liquid whose pigment content in a microencapsulation pigment is 67%)

In the example 1, it replaced with the anionic microencapsulation pigment content aqueous dispersion  
 liquid (MC-2) of the copper phthalocyanine blue obtained in the example 2 of manufacture, and the  
 recording ink of a yellow color was prepared like the example 1 except having used the anionic  
 microencapsulation pigment content aqueous dispersion liquid (MC-13) of the yellow color obtained in  
 the example 13 of manufacture.

[0186] In examples 1, 2, and 3, since in preparing recording ink dispersers, such as a bead mill and a roll,  
 were not needed but it prepared only by only mixing especially, while a distributed facility is unnecessary,  
 can shorten a distributed process and an effort, being able to perform compaction of production time, or  
 laborsaving of distributed energy and raising productivity greatly, a manufacturing cost is reducible.  
 Moreover, the pigment content in aqueous dispersion liquid was also as high as 13.4% or more, the  
 pigment content in an anionic microencapsulation pigment is as high as 67%, and versatility was [ the  
 anionic microencapsulation pigment content aqueous dispersion liquid used for these could add other  
 ingredients, such as water soluble resin used in order to improve the engine performance as recording  
 ink, and a water-soluble organic solvent in most amount, and ] high [ dispersion liquid ].

[0187] Next, the volume mean particle diameter after storing at a room temperature, and the  
 sedimentation nature of a particle were shown in Table 4 for the volume mean particle diameter of the  
 microencapsulation pigment in the recording ink of these cyanogen color, a Magenta color, and a yellow  
 color, and 30 days. It is before and after storage, an almost equivalent value is shown, and  
 sedimentation of a particle is not seen further, but it is clear volume mean particle diameter's of the  
 anionic microencapsulation pigment in each recording ink obtained in the examples 1, 2, and 3 to excel  
 in storage stability and distributed stability very much compared with the conventional  
 microencapsulation pigment.

[0188] Next, the color record image of a cyanogen color, a Magenta color, and a yellow color was  
 recorded on an OHP sheet and copy paper using the printer of commercial Bubble Jet using the  
 above-mentioned recording ink. As shown in Table 6, this record image had definition and the high  
 depth of shade, and they were excellent in color rendering properties or transparency. Moreover, since

the image recorded on the OHP sheet was excellent in transparency, it showed colorful projection drawing. It did not disappear, even if it attached water and ground the record image on an OHP sheet, and it excelled also in the water resisting property. Moreover, even if it used it repeatedly, the nozzle which makes ink breathe out was not got blocked.

[0189] <The example 1 of a comparison> (manufacture of the recording ink with which the mean particle diameter of a microencapsulation pigment used the microencapsulation pigment dispersion liquid to which the maximum particle diameter exceeds 1000nm by 650nm)

In the example 1, it replaced with the anionic microencapsulation pigment content aquosity dispersion liquid (MC-2) of the copper phthalocyanine blue obtained in the example 2 of manufacture, and the recording ink of a cyanogen color was prepared like the example 1 except having used the anionic microencapsulation pigment content aquosity dispersion liquid (MC-5) of the copper phthalocyanine blue obtained in the example 5 of manufacture.

[0190] The volume mean particle diameter after storing at a room temperature, and the sedimentation nature of a particle were shown in Table 8 for the volume mean particle diameter of the microencapsulation pigment in the recording ink of the cyanogen color obtained in the example 1 of a comparison, and 30 days. Although the volume mean particle diameter of the anionic microencapsulation pigment in the recording ink of this example of a comparison is before and after storage and showed the almost equivalent value, sedimentation of a particle was seen and its distributed stability was bad.

[0191] Next, the color record image of a cyanogen color was recorded on an OHP sheet and copy paper using the commercial bubble-jet printer using the above-mentioned recording ink. As shown in Table 9, this record image had definition and the low depth of shade, and they lacked in color rendering properties or transparency. Moreover, the image recorded on the OHP sheet did not show opaque and colorful projection drawing, and was not able to use it for the OHP sheet. Moreover, while using it repeatedly, the nozzle which makes ink breathe out was got blocked and use of a printer became impossible.

[0192] <Example 4> (manufacture of the recording ink which used the microencapsulation pigment dispersion liquid whose pigment content in a microencapsulation pigment is 51.7%)

In the anionic microencapsulation pigment content aquosity dispersion-liquid (MC-1) 47.4 section of the copper phthalocyanine blue obtained in the example 1 of manufacture, the ethylene glycol 20 section, the diethanolamine 3.0 section, and the ion-exchange-water 29.6 section were mixed, and the pigment content prepared the recording ink of 6% of cyanogen color in it.

[0193] <Example 5> (manufacture of the recording ink which used the microencapsulation pigment dispersion liquid whose pigment content in a microencapsulation pigment is 51.7%)

In the anionic microencapsulation pigment content aquosity dispersion-liquid (MC-6) 50.0 section of the Magenta color obtained in the example 6 of manufacture, the ethylene glycol 20 section, the diethanolamine 3.0 section, and the ion-exchange-water 27.0 section were mixed, and the pigment content prepared the recording ink of 6% of Magenta color in it.

[0194] <Example 6> (manufacture of the recording ink which used the microencapsulation pigment dispersion liquid whose pigment content in a microencapsulation pigment is 51.7%)

In the anionic microencapsulation pigment content aquosity dispersion-liquid (MC-12) 48.8 section of the yellow color obtained in the example 12 of manufacture, the ethylene glycol 20 section, the diethanolamine 3.0 section, and the ion-exchange-water 28.2 section were mixed, and the pigment content prepared the recording ink of 6% of yellow color in it.

[0195] In these examples 4, 5, and 6, since in preparing recording ink dispersers, such as a bead mill and a roll, were not needed but it prepared only by only mixing especially, while a distributed facility is unnecessary, can shorten a distributed process and an effort, being able to perform compaction of production time, or laborsaving of distributed energy and raising productivity greatly, a manufacturing

cost is reducible. Moreover, the pigment content in aqueous dispersion liquid was also as high as 10% or more, the pigment content in an anionic microencapsulation pigment is as high as 51.7%, and versatility was [ the anionic microencapsulation pigment content aqueous dispersion liquid used for these could add other ingredients, such as a water-soluble organic solvent used in order to improve the engine performance as recording ink, in most amount, and ] high [ dispersion liquid ].

[0196] The volume mean particle diameter after storing at a room temperature, and the sedimentation nature of a particle were shown in Table 4 for the volume mean particle diameter of the microencapsulation pigment in the recording ink of these cyanogen color, a Magenta color, and a yellow color, and 30 days. It is before and after storage, an almost equivalent value is shown, and sedimentation of a particle is not seen further, but it is clear volume mean particle diameter's of the anionic microencapsulation pigment in the recording ink of this example to excel in storage stability and distributed stability very much compared with the conventional microencapsulation pigment.

[0197] Next, the color record image of a cyanogen color, a Magenta color, and a yellow color was recorded on an OHP sheet and copy paper using the ink jet printer of a commercial piezo method using the above-mentioned recording ink. As shown in Table 6, this record image had definition and the high depth of shade, and they were excellent in color rendering properties or transparency. Moreover, since the image recorded on the OHP sheet was excellent in transparency, it showed colorful projection drawing. It did not disappear, even if it attached water and ground the record image on an OHP sheet, and it excelled also in the water resisting property. Moreover, even if it used it repeatedly, the nozzle which makes ink breathe out was not got blocked.

[0198] <Example 7> (manufacture of the recording ink which used the microencapsulation pigment dispersion liquid whose pigment content in a microencapsulation pigment is 67%)

In the anionic microencapsulation pigment content aqueous dispersion-liquid (MC-2) 44.8 section of the copper phthalocyanine blue obtained in the example 2 of manufacture, the aqueous ammonia solution 5.0 section (equivalent to the resin solid content 2.5 section) of styrene acrylic acid resin of 50% of nonvolatile matters of the acid number 163 and molecular weight 25,000, the ethylene glycol 20 section, the diethanolamine 3.0 section, and the ion-exchange-water 27.2 section were mixed, and the pigment content prepared the recording ink of 6% of cyanogen color in it.

[0199] <Example 8> (manufacture of the recording ink which used the microencapsulation pigment dispersion liquid whose pigment content in a microencapsulation pigment is 67%)

In the example 7, it replaced with the anionic microencapsulation pigment content aqueous dispersion liquid (MC-2) of the copper phthalocyanine blue obtained in the example 2 of manufacture, and the recording ink of a Magenta color was prepared like the example 7 except having used the anionic microencapsulation pigment content aqueous dispersion liquid (MC-7) of the Magenta color obtained in the example 7 of manufacture.

[0200] <Example 9> (manufacture of the recording ink which used the microencapsulation pigment dispersion liquid whose pigment content in a microencapsulation pigment is 67%)

In the example 7, it replaced with the anionic microencapsulation pigment content aqueous dispersion liquid (MC-2) of the copper phthalocyanine blue obtained in the example 2 of manufacture, and the recording ink of a yellow color was prepared like the example 7 except having used the anionic microencapsulation pigment content aqueous dispersion liquid (MC-13) of the yellow color obtained in the example 13 of manufacture.

[0201] <Example 10> (manufacture of the recording ink which used the microencapsulation pigment dispersion liquid whose pigment content in a microencapsulation pigment is 75%)

The aqueous ammonia solution 5.0 section (equivalent to the resin solid content 2.5 section) of the styrene acrylic acid resin used for the anionic microencapsulation pigment content aqueous dispersion-liquid (MC-9) 40.0 section of the Magenta color obtained in the example 9 of manufacture in the example 7, the ethylene glycol 20 section, the diethanolamine 3.0 section, and the



ion-exchange-water 32.0 section were mixed, and the pigment content prepared the recording ink of 6% of Magenta color.

[0202] <Example 11> (manufacture of the recording ink which used the microencapsulation pigment dispersion liquid whose pigment content in a microencapsulation pigment is 67%)

In the example 7, it replaced with the anionic microencapsulation pigment content aqueous dispersion liquid (MC-2) of the copper phthalocyanine blue obtained in the example 2 of manufacture, and the recording ink of a cyanogen color was prepared like the example 7 except having used the anionic microencapsulation pigment content aqueous dispersion liquid (MC-4) of the copper phthalocyanine blue obtained in the example 4 of manufacture.

[0203] In examples 7, 8, 9, 10, and 11, since in preparing recording ink dispersers, such as a bead mill and a roll, were not needed but it prepared only by only mixing especially, while a distributed facility is unnecessary, can shorten a distributed process and an effort, being able to perform compaction of production time, or laborsaving of distributed energy and raising productivity greatly, a manufacturing cost is reducible. Moreover, the pigment content in aqueous dispersion liquid was also as high as 13.4% or more, the pigment content in an anionic microencapsulation pigment is as high as 67% or more, and versatility was [ the anionic microencapsulation pigment content aqueous dispersion liquid used for these could add other ingredients, such as water soluble resin used in order to improve the engine performance as recording ink, and a water-soluble organic solvent, in most amount, and ] high [ dispersion liquid ].

[0204] The volume mean particle diameter after storing at a room temperature, and the sedimentation nature of a particle were shown in Table 5 for the volume mean particle diameter of the microencapsulation pigment in the recording ink of these cyanogen color, a Magenta color, and a yellow color, and 30 days. It is before and after storage, an almost equivalent value is shown, and sedimentation of a particle is not seen further, but it is clear volume mean particle diameter's of the anionic microencapsulation pigment in the recording ink of this example to excel in storage stability and distributed stability very much compared with the conventional microencapsulation pigment.

[0205] Next, the color record image of a cyanogen color, a Magenta color, and a yellow color was recorded on an OHP sheet and copy paper using the ink jet printer of a commercial piezo method using the above-mentioned recording ink. As shown in Tables 6 and 7, this record image had definition and the high depth of shade, and they were excellent in color rendering properties or transparency. Moreover, since the image recorded on the OHP sheet was excellent in transparency, it showed colorful projection drawing. It did not disappear, even if it attached water and ground the record image on an OHP sheet, and it excelled also in the water resisting property. Moreover, even if it used it repeatedly, the nozzle which makes ink breathe out was not got blocked.

[0206] <The example 2 of a comparison> (manufacture of the recording ink which used the microencapsulation pigment dispersion liquid whose pigment content in a microencapsulation pigment is 33%)

The aqueous ammonia solution 5.0 section (equivalent to the resin solid content 2.5 section) of the styrene acrylic acid resin used for the anionic microencapsulation pigment content aqueous dispersion-liquid (MC-10) 90.1 section of the Magenta color obtained in the example 10 of manufacture in the example 7, the ethylene glycol 1.9 section, and the diethanolamine 3.0 section were mixed, and the pigment content prepared the recording ink of 6% of Magenta color.

[0207] The anionic microencapsulation pigment content aqueous dispersion liquid used for this had the pigment content as low as 33% in an anionic microencapsulation pigment, and its pigment content in aqueous dispersion liquid was also as low as 6.6%, and they were what a limitation is in the addition of other ingredients, such as water soluble resin used in order to improve the engine performance as recording ink, and a water-soluble organic solvent, with the depth of shade of recording ink maintained, and lacks in versatility. Moreover, since there were many amounts of resin used for a microcapsule, the

problem arose in compatibility with other ingredients.

[0208] The volume mean particle diameter after storing at a room temperature, and the sedimentation nature of a particle were shown in Table 8 for the volume mean particle diameter of the microencapsulation pigment in the recording ink of this Magenta color, and 30 days. It is before and after storage, the almost equivalent value was shown, and sedimentation of a particle was not seen further, but the volume mean particle diameter of the anionic microencapsulation pigment in the recording ink of this example of a comparison was very excellent in storage stability and distributed stability.

[0209] Next, the color record image of a Magenta color was recorded on an OHP sheet and copy paper using the ink jet printer of a commercial piezo method using the above-mentioned recording ink. Since there were few additions of the ethylene glycol in recording ink, it produced a blot and flipping to copy paper or an OHP sheet, and as the record image was shown in Table 9, definition was low and color rendering properties and transparency were missing. Moreover, the image recorded on the OHP sheet did not show opaque and colorful projection drawing, and was not able to use it for the OHP sheet. It did not disappear, even if it attached water and ground the record image on an OHP sheet, and it excelled in the water resisting property. Moreover, when it was used repeatedly, the nozzle which makes ink breathe out might be got blocked.

[0210] <The example 3 of a comparison> (manufacture of the recording ink which used the microencapsulation pigment dispersion liquid whose pigment content in a microencapsulation pigment is 83%)

The aqueous ammonia solution 5.0 section (equivalent to the resin solid content 2.5 section) of the styrene acrylic acid resin used for the anionic microencapsulation pigment content aqueous dispersion-liquid (MC-8) 36.1 section of the Magenta color obtained in the example 8 of manufacture in the example 7, the ethylene glycol 20 section, the diethanolamine 3.0 section, and the ion-exchange-water 35.9 section were mixed, and the pigment content prepared the recording ink of 6% of Magenta color.

[0211] The volume mean particle diameter after storing at a room temperature, and the sedimentation nature of a particle were shown in Table 8 for the volume mean particle diameter of the microencapsulation pigment in the recording ink of this Magenta color, and 30 days. Since the anionic microencapsulation pigment in the recording ink of this example of a comparison had low resin concentration, a pigment was not made as for things to maintaining at stability in the detailed condition, but a lifting and volume mean particle diameter became large about the condensation after storage, sedimentation of a particle was also seen, and the anionic microencapsulation pigment had storage stability and bad distributed stability.

[0212] Next, the color record image of a Magenta color was recorded on an OHP sheet and copy paper using the ink jet printer of a commercial piezo method using the above-mentioned recording ink. Since the capsule had caused condensation, as shown in Table 9, this record image had definition and the low depth of shade, and they lacked in color rendering properties or transparency. Moreover, the image recorded on the OHP sheet did not show opaque and colorful projection drawing, and was not able to use it for the OHP sheet. Moreover, while using it repeatedly, the nozzle which makes ink breathe out was got blocked and use of a printer became impossible.

[0213] <The example 4 of a comparison> (manufacture of the recording ink with which the mean particle diameter of a microencapsulation pigment used the microencapsulation pigment dispersion liquid to which the maximum particle diameter exceeds 1000nm by 650nm)

The aqueous ammonia solution 5.0 section (equivalent to the resin solid content 2.5 section) of the styrene acrylic acid resin used for the anionic microencapsulation pigment content aqueous dispersion-liquid (MC-5) 44.8 section of the copper phthalocyanine blue obtained in the example 5 of manufacture in the example 7, the ethylene glycol 20 section, the diethanolamine 3.0 section, and the ion-exchange-water 27.2 section were mixed, and the pigment content prepared the recording ink of 6%

of cyanogen color.

[0214] The volume mean particle diameter after storing at a room temperature, and the sedimentation nature of a particle were shown in Table 8 for the volume mean particle diameter of the microencapsulation pigment in the recording ink of this cyanogen color, and 30 days. Although the volume mean particle diameter of the anionic microencapsulation pigment in the recording ink of this example of a comparison is before and after storage and showed the almost equivalent value, sedimentation of a particle was seen and storage stability and its distributed stability were bad.

[0215] Next, the color record image of a cyanogen color was recorded on an OHP sheet and copy paper using the ink jet printer of a commercial piezo method using the above-mentioned recording ink. As shown in Table 9, this record image had definition and the low depth of shade, and they lacked in color rendering properties or transparency. Moreover, the image recorded on the OHP sheet did not show opaque and colorful projection drawing, and was not able to use it for the OHP sheet. Moreover, while using it repeatedly, the nozzle which makes ink breathe out was got blocked and use of a printer became impossible.

[0216] <The example 5 of a comparison> (manufacture of the recording ink which used the microencapsulation pigment dispersion liquid to which the mean particle diameter of an organic pigment exceeds 200nm)

The aqueous ammonia solution 5.0 section (equivalent to the resin solid content 2.5 section) of the styrene acrylic acid resin used for the anionic microencapsulation pigment content aquosity dispersion-liquid (MC-11) 44.8 section of the Magenta color obtained in the example 11 of manufacture in the example 7, the ethylene glycol 20 section, the diethanolamine 3.0 section, and the ion-exchange-water 27.2 section were mixed, and the pigment content prepared the recording ink of 6% of Magenta color.

[0217] The volume mean particle diameter after storing at a room temperature, and the sedimentation nature of a particle were shown in Table 8 for the volume mean particle diameter of the microencapsulation pigment in the recording ink of this Magenta color, and 30 days. It is before and after storage, the almost equivalent value was shown, and sedimentation of a particle was not seen, but the volume mean particle diameter of the anionic microencapsulation pigment in the recording ink of this example of a comparison was excellent in storage stability and distributed stability.

[0218] Next, the color record image of a Magenta color was recorded on an OHP sheet and copy paper using the ink jet printer of a commercial piezo method using the above-mentioned recording ink. As shown in Table 9, this record image had definition and the low depth of shade, and they lacked in color rendering properties or transparency. Especially the image recorded on the OHP sheet did not show opaque and colorful projection drawing, and was not able to use it for the OHP sheet. Moreover, even if it used it repeatedly, the nozzle which makes ink breathe out was not got blocked.

[0219] <The example 6 of a comparison> (manufacture of the recording ink which used the microencapsulation pigment dispersion liquid to which the mean particle diameter of an organic pigment exceeds 200nm)

The aqueous ammonia solution 5.0 section (equivalent to the resin solid content 2.5 section) of the styrene acrylic acid resin used for the anionic microencapsulation pigment content aquosity dispersion-liquid (MC-14) 44.8 section of the yellow color obtained in the example 14 of manufacture in the example 7, the ethylene glycol 20 section, the JIETANORU amine 3.0 section, and the ion-exchange-water 27.2 section were mixed, and the pigment content prepared the recording ink of 6% of yellow color.

[0220] The volume mean particle diameter after storing at a room temperature, and the sedimentation nature of a particle were shown in Table 8 for the volume mean particle diameter of the microencapsulation pigment in the recording ink of this yellow color, and 30 days. It is before and after storage, the almost equivalent value was shown, and sedimentation of a particle was not seen, but the

volume mean particle diameter of the anionic microencapsulation pigment in the recording ink of this example of a comparison was excellent in storage stability and distributed stability.

[0221] Next, the color record image of a Magenta color was recorded on an OHP sheet and copy paper using the ink jet printer of a commercial piezo method using the above-mentioned recording ink. As shown in Table 9, this record image had definition and the low depth of shade, and they lacked in color rendering properties or transparency. Especially the image recorded on the OHP sheet did not show opaque and colorful projection drawing, and was not able to use it for the OHP sheet. Moreover, even if it used it repeatedly, the nozzle which makes ink breathe out was not got blocked.

[0222] <Example 12> (manufacture of the recording ink which used the microencapsulation pigment dispersion liquid of the base of a non-volatile)

In the anionic microencapsulation pigment content aqueous dispersion-liquid (MC-15) 37.5 section of the copper phthalocyanine blue obtained in the example 15 of manufacture, the ethylene glycol 5 section, the glycerol 10.0 section, the diethanolamine 3.0 section, and the ion-exchange-water 44.5 section were mixed, and the pigment content prepared the recording ink of 5.0% of cyanogen color in it.

[0223] <Example 13> (manufacture of the recording ink which used the microencapsulation pigment dispersion liquid of the base of a non-volatile)

In the example 12, it replaced with the anionic microencapsulation pigment content aqueous dispersion liquid (MC-15) of the copper phthalocyanine blue obtained in the example 15 of manufacture, and the recording ink of a Magenta color was prepared like the example 12 except having used the anionic microencapsulation pigment content aqueous dispersion liquid (MC-16) of the Magenta color obtained in the example 16 of manufacture.

[0224] <Example 14> (manufacture of the recording ink which used the microencapsulation pigment dispersion liquid of the base of a non-volatile)

In the example 12, it replaced with the anionic microencapsulation pigment content aqueous dispersion liquid (MC-15) of the copper phthalocyanine blue obtained in the example 15 of manufacture, and the recording ink of a yellow color was prepared like the example 12 except having used the anionic microencapsulation pigment content aqueous dispersion liquid (MC-17) of the yellow color obtained in the example 17 of manufacture.

[0225] In examples 12, 13, and 14, since in preparing recording ink dispersers, such as a bead mill and a roll, were not needed but it prepared only by only mixing especially, while a distributed facility is unnecessary, can shorten a distributed process and an effort, being able to perform compaction of production time, or laborsaving of distributed energy and raising productivity greatly, a manufacturing cost is reducible. Moreover, the pigment content in aqueous dispersion liquid was also as high as 13.4% or more, the pigment content in an anionic microencapsulation pigment is as high as 67%, and versatility was [ the anionic microencapsulation pigment content aqueous dispersion liquid used for these could add other ingredients, such as water soluble resin used in order to improve the engine performance as recording ink, and a water-soluble organic solvent in most amount, and ] high [ dispersion liquid ].

[0226] Next, the volume mean particle diameter after storing at a room temperature, and the sedimentation nature of a particle were shown in Table 5 for the volume mean particle diameter of the microencapsulation pigment in the recording ink of these cyanogen color, a Magenta color, and a yellow color, and 30 days. It is before and after storage, an almost equivalent value is shown, and sedimentation of a particle is not seen further, but it is clear volume mean particle diameter's of the anionic microencapsulation pigment in each recording ink obtained in the examples 12, 13, and 14 to excel in storage stability and distributed stability very much compared with the conventional microencapsulation pigment.

[0227] Next, the color record image of a cyanogen color, a Magenta color, and a yellow color was recorded on an OHP sheet and copy paper using the printer of a commercial piezo method using the above-mentioned recording ink. As shown in Table 7, these record images had definition and the high

depth of shade, and they were excellent in color rendering properties or transparency. Moreover, since this record image was excellent in transparency, it showed colorful projection drawing. Furthermore, when water was attached and the record image on an OHP sheet was \*\* (ed), it was easy to disappear, but even if it hung down several drops of water to the record image in the copy paper, it spread, a record image did not disappear and it excelled also in the water resisting property.

[0228] Moreover, since the count of cleaning was managed with less than 3 times compared with the case where an volatile amine is used when it was cleaned and used after leaving the nozzle which packed the ink of these cyanogen colors, a Magenta color, and a yellow color for 15 days at a room temperature, it excelled in redispersible [ of ink ] very much.

[0229] <Example 15> (manufacture of the recording ink which used the microencapsulation pigment dispersion liquid which carried out gelation processing)

In the anionic microencapsulation pigment content aqueous dispersion-liquid (MC-18) 37.5 section of the carbon black obtained in the example 18 of manufacture, the ethylene glycol 5 section, the glycerol 10.0 section, the diethanolamine 3.0 section, and the ion-exchange-water 44.5 section were mixed, and the pigment content prepared the recording ink of 5.0% of carbon black in it.

[0230] Next, the volume mean particle diameter after storing at a room temperature, and the sedimentation nature of a particle were shown in Table 5 for the volume mean particle diameter of the microencapsulation pigment in the recording ink of this carbon black, and 30 days. It is before and after storage, an almost equivalent value is shown, and sedimentation of a particle is not seen further, but it is clear volume mean particle diameter's of the anionic microencapsulation pigment in this recording ink to excel in storage stability and distributed stability very much compared with the conventional microencapsulation pigment.

[0231] Next, the record image of a BURRAKU color was recorded on an OHP sheet and copy paper using the ink jet printer of a commercial piezo method using the above-mentioned recording ink. As shown in Table 7, these record images had a Japanese lacquer black tint, and definition and its depth of shade were high. Furthermore, it was it hard to disappear to attach water and to \*\* the record image on an OHP sheet, and excelled also in the water resisting property.

[0232] Moreover, when it was cleaned and used after leaving the nozzle which packed this recording ink for 15 days at a room temperature, since the count of cleaning was managed with 6 times, it excelled also in redispersible [ of ink ].

[0233] Furthermore, when this recording ink was put into the glass bottle, and was sealed and the thermostat performed the resistance to solvents test for ten days at 80 degrees C, it excelled very much, without volume mean particle diameter being changeless and condensing compared with 189nm and trial before.

[0234] <Example 16> (manufacture of the recording ink which used the microencapsulation pigment dispersion liquid of the base of a non-volatile)

The aqueous ammonia solution 5.0 section (equivalent to the resin solid content 2.5 section) of the styrene acrylic acid resin used for the anionic microencapsulation pigment content aqueous dispersion-liquid (MC-3) 44.8 section of the copper phthalocyanine blue obtained in the example 3 of manufacture in the example 7, the ethylene glycol 20 section, the diethanolamine 3.0 section, and the ion-exchange-water 27.2 section were mixed, and the pigment content prepared the recording ink of 6% of cyanogen color.

[0235] The volume mean particle diameter after storing at a room temperature, and the sedimentation nature of a particle were shown in Table 5 for the volume mean particle diameter of the microencapsulation pigment in the recording ink of this cyanogen color, and 30 days. It is before and after storage, the almost equivalent value was shown, and sedimentation of a particle was not seen, but the volume mean particle diameter of the anionic microencapsulation pigment in the recording ink of this example of a comparison was excellent in storage stability and distributed stability.

[0236] Next, the color record image of a cyanogen color was recorded on an OHP sheet and copy paper using the ink jet printer of a commercial piezo method using the above-mentioned recording ink. As shown in Table 7, this record image had definition and the high depth of shade, and they were excellent in color rendering properties or transparency. Projection drawing transparent [ especially the image recorded on the OHP sheet ] and colorful was shown. Furthermore, when water was attached and the record image on an OHP sheet was \*\* (ed), it was easy to disappear, but even if it hung down several drops of water to the record image in the copy paper, it spread, a record image did not disappear and it excelled also in the water resisting property.

[0237] Moreover, when it was cleaned and used after leaving the nozzle which packed the recording ink of this cyanogen color for 15 days at a room temperature, since the count of cleaning was managed with less than 3 times, it excelled in redispersible [ of ink ] very much.

[0238]

[Table 4]

	マイクロカプセル化顔料含有水性分散液	体積平均径 (nm)		沈降性
		貯蔵前	貯蔵後	
実施例 1	MC-2	175	180	○
実施例 2	MC-7	182	186	○
実施例 3	MC-13	192	190	○
実施例 4	MC-1	152	155	○
実施例 5	MC-6	143	148	○
実施例 6	MC-12	182	179	○
実施例 7	MC-2	176	183	○
実施例 8	MC-7	173	172	○
実施例 9	MC-13	183	192	○
実施例 10	MC-9	185	189	○

[0239]

[Table 5]

	マイクロカプセル化顔料含有水性分散液	体積平均径(nm)		沈降性
		貯蔵前	貯蔵後	
実施例11	MC-4	225	221	○
実施例12	MC-15	158	154	○
実施例13	MC-16	182	174	○
実施例14	MC-17	188	193	○
実施例15	MC-18	153	147	○
実施例16	MC-3	172	171	○

[0240] The cable address in Tables 4 and 5, the evaluation approach, and the valuation basis are as follows.

Volume mean diameter : volume mean particle diameter of an anionic microencapsulation pigment (nm)

Sedimentation nature : [0241] as which sedimentation condition O= fitness x= sedimentation of the particle after storage is regarded

[Table 6]

	マイクロカプセル化顔料含有水性分散液	ジェットプリンタの種類	再分散性	記録画像			
				耐水性	精細度	色濃度	透明性
実施例1	MC-2	BJ	—	○	○	○	○
実施例2	MC-7	BJ	—	○	○	○	○
実施例3	MC-13	BJ	—	○	○	○	○
実施例4	MC-1	PJ	△	○	○	○	○
実施例5	MC-6	PJ	△	○	○	○	○
実施例6	MC-12	PJ	△	○	○	○	○
実施例7	MC-2	PJ	△	○	○	○	○
実施例8	MC-7	PJ	△	○	○	○	○
実施例9	MC-13	PJ	△	○	○	○	○
実施例10	MC-9	PJ	△	○	○	○	○



[0242]  
[Table 7]

	マイクロカプセル化顔料含有水性分散液	ジェットプリンタの種類	再分散性	記録画像			
				耐水性	精細度	色濃度	透明性
実施例11	MC-4	PJ	△	○	○	○	○
実施例12	MC-15	PJ	○	△	○	○	○
実施例13	MC-16	PJ	○	△	○	○	○
実施例14	MC-17	PJ	○	△	○	○	○
実施例15	MC-18	PJ	△	○	○	○	-
実施例16	MC-3	PJ	○	△	○	○	○

[0243] The cable address in Tables 6 and 7, the evaluation approach, and the valuation basis are as follows.

BJ : ink jet printer of Bubble Jet PJ : Ink jet printer of a piezo method Redispersible : While it had been filled up with ink, it prints again after leaving it in mesoecium for 15 days at a room temperature, and easy estimates.

O = cleaning is printable within 3 times. \*\* = cleaning 4 - 9 times More than x=10 time - : Un-evaluating.

Water resisting property : An O=OHP sheet does not disappear, either. In \*\* = copy paper, a blot [ little ] It permeates in x= copy paper and a record image cannot be read. Definition : O= fitness x = it is bad.

Depth of shade : O = it is high. x = it is low. Transparency : O = transparence x = opacity [0244]

[Table 8]

	マイクロカプセル化顔料含有水性分散液	体積平均径(μm)		沈降性
		貯蔵前	貯蔵後	
比較例1	MC-5	570	581	×
比較例2	MC-7	230	235	○
比較例3	MC-13	735	1259	×
比較例4	MC-5	690	770	×
比較例5	MC-1	290	307	○
比較例6	MC-6	257	265	○

[0245] The cable address in Table 8, the evaluation approach, and the valuation basis are as follows.  
 Volume mean diameter : volume mean particle diameter of an anionic microencapsulation pigment (nm)  
 Sedimentation nature : [0246] as which sedimentation condition O= fitness x= sedimentation of the particle after storage is regarded  
 [Table 9]

	マイクロカプセル化顔料含有水性分散液	ジェットプリンタの種類	再分散性	記録画像			
				耐水性	精細度	色濃度	透明性
比較例 1	MC-5	BJ	-	-	×	×	×
比較例 2	MC-10	PJ	-	○	×	×	×
比較例 3	MC-8	PJ	-	-	×	×	×
比較例 4	MC-5	PJ	-	-	×	×	×
比較例 5	MC-11	PJ	-	-	×	×	×
比較例 6	MC-14	PJ	-	-	×	×	×

[0247] The cable address in Table 9, the evaluation approach, and the valuation basis are as follows.  
 BJ : ink jet printer of Bubble Jet PJ : Ink jet printer of a piezo method Redispersible : While it had been filled up with ink, it prints again after leaving it in mesoecium for 15 days at a room temperature, and easy estimates.

O = cleaning is printable within 3 times. \*\* = cleaning 4 - 9 times More than x=10 time - : un-evaluating.  
 Water resisting property : An O=OHP sheet does not disappear, either. In \*\* = copy paper, a blot [ little ] It permeates in x= copy paper and a record image cannot be read. Definition : O= fitness x = it is bad.  
 Depth of shade : O = it is high. x = it is low. Transparency : O= transperence x= opacity [0248]

[Effect of the Invention] The anionic microencapsulation pigment content aquosity dispersion liquid for recording ink of this invention are a very fine pigment dispersing element, and since it excels in storage stability, definition and its depth of shade are high, are excellent in color rendering properties or transparency, and they can aim at reduction of a manufacturing cost and the cost of recording ink by laborsaving of a distributed process. Moreover, since the pigment content is high, in case the anionic microencapsulation pigment content aquosity dispersion liquid for recording ink of this invention are processed into recording ink, it is possible on a formula to be able to use various ingredients, and they have the advantage that versatility is high.

[0249] Furthermore, since it excels in redispersible by using the base of a non-volatile, there is an advantage that the dependability of recording ink increases.

## TECHNICAL FIELD

[Field of the Invention] the recording ink containing an anionic microencapsulation pigment with the high pigment concentration in a microencapsulation pigment useful as an ingredient for this invention to manufacture the aquosity recording ink for ink jet printers on demand type [, such as writing implements,

such as an aqueous ball-point, a fountain pen, an aqueous felt-tipped marker, and an aqueous marker, Bubble Jet and a thermal jet method, and a piezo method, ] -- service water -- it is related with sex dispersion liquid and the recording ink containing the dispersion liquid.

## PRIOR ART

[Description of the Prior Art] Conventionally, the color has been used for the recording ink of which a high definition is required. Although the recording ink using a color has the descriptions, such as high transparency, a high definition, and outstanding color rendering properties, it has problems, such as lightfastness and a water resisting property.

[0003] In order to solve lightfastness and a waterproof problem in recent years, it replaces with a color and the recording ink using an organic pigment or carbon black is manufactured.

[0004] However, if distributed stabilization of the pigment is not carried out very finely when an organic pigment and carbon black are used, there is a trouble that a high definition and advanced color rendering properties cannot be acquired as recording ink. Especially, in the recording ink for ink jet printers, if distributed stabilization of the pigment is not carried out very finely, it will link with the trouble of the blinding of a nozzle directly. Moreover, if the pigment was distributed minutely and high transparency was not secured when an organic pigment was used for the application of the OHP sheet projected with a back light, there was a trouble that the projection image of colorful OHP was not obtained.

[0005] Compared with the organic pigments and carbon black which are generally used, such as a coating and ink, especially the organic pigment and carbon black that are used for these have a fine diameter of a primary particle, and since secondary condensation is strong, they need great energy for distributing these pigments even to a primary particle. Moreover, various devices are required to maintain the pigment in dispersion liquid at stability even if it is able to distribute these pigments to a primary particle.

[0006] In order to solve these troubles, as shown below, the approach of using a microcapsule is indicated. for example, to JP,62-95366,A To the approach and JP,1-170672,A which use for recording ink the microcapsule which connoted color ink in the polymer particle Make water dissolve or distribute coloring matter to an insoluble solvent substantially, and emulsification distribution of this is underwater carried out using a surfactant. To the approach and JP,5-39447,A which use for recording ink the coloring matter which microencapsulated by the conventional technique The approach the endocyst object of a microcapsule uses water and the microcapsule which made the water-soluble solvent list dissolve or distribute a sublimability disperse dye to at least one sort of polyester resin for a record constituent, The water-color-ink constituent which becomes JP,6-313141,A from the colored emulsion-polymerization particle and various aqueous ingredients is indicated.

## EFFECT OF THE INVENTION

[Effect of the Invention] The anionic microencapsulation pigment content aqueous dispersion liquid for recording ink of this invention are a very fine pigment dispersing element, and since it excels in storage stability, definition and its depth of shade are high, are excellent in color rendering properties or transparency, and they can aim at reduction of a manufacturing cost and the cost of recording ink by laborsaving of a distributed process. Moreover, since the pigment content is high, in case the anionic microencapsulation pigment content aqueous dispersion liquid for recording ink of this invention are processed into recording ink, it is possible on a formula to be able to use various ingredients, and they have the advantage that versatility is high.

[0249] Furthermore, since it excels in redispersible by using the base of a non-volatile, there is an advantage that the dependability of recording ink increases.

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## TECHNICAL PROBLEM

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[Problem(s) to be Solved by the Invention] However, it had the trouble that that of what encapsulated the color was inferior to lightfastness, and since the microencapsulation pigment manufactured by the conventional approach had a large particle size, it had the trouble of being inferior to transparency, color enhancement, color rendering properties, etc. Moreover, since the resin concentration in a capsule was high (pigment concentration is low), the selectivity of the ingredient used for recording ink was small, versatility was missing, and the recording ink had further the trouble that a feeling of concentration was lost. furthermore, the thing for which a detailed microencapsulation pigment is manufactured only by resin when pigment concentration is made high too much -- difficult -- so -- a surfactant -- not using together -- it was not that from which the record image with which it does not obtain, therefore is not necessarily satisfied of a water resisting property is obtained.

[0008] In manufacture of the recording ink with which the pigment dispersion liquid of a drainage system were used for the technical problem which this invention tends to solve Laborsaving of the process which distributes a pigment minutely on the dispersion-medium object of recording ink is realized, a great effort, a facility, energy, etc. are saved labor, and the microencapsulation pigment content aqueous dispersion liquid which can reduce the manufacturing cost of recording ink are offered, Moreover, the thing for which the microencapsulation pigment content aqueous dispersion liquid for recording ink with the high versatility excellent in the degree of freedom of selections, such as resin for recording ink, various additives, or a solvent, are offered, Furthermore, it is in offering the recording ink using a feeling of concentration, a high definition, the color rendering properties and transparency that are required of recording ink, and the microencapsulation pigment content aqueous dispersion liquid and these aqueous dispersion liquid for recording ink which were further excellent in a water resisting property, redispersible, etc.

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## MEANS

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[Means for Solving the Problem] It is anionic microencapsulation pigment content aqueous dispersion liquid which cover an organic pigment or carbon black with anionic radical content organic high molecular compounds as a result of repeating examination, and change wholeheartedly that this invention persons should solve the above-mentioned technical problem. When the anionic microencapsulation pigment content aqueous dispersion liquid in the range the organic pigment in an anionic microencapsulation pigment or whose content of carbon black is 35 - 80 % of the weight are processed into recording ink, Since it can be used only by there being neither selection of the resin at the time of manufacture, a solvent, or various additives nor a limit of an addition, and versatility being raised, and mixing anionic microencapsulation pigment content aqueous dispersion liquid further, Since it is not necessary to carry out indispensable use of that reducing the conventional manufacturing cost, the definition of recording ink, and color rendering properties and transparency can be improved more than before, and the surfactant Raising the water resisting property of a record image, that raise redispersible and the dependability of recording ink is raised by using the thing (alkali metal) of a non-volatile for the base for neutralization of the anionic radical content organic high molecular compounds which are resin for microencapsulating further, etc. A header, It came to complete this invention.

[0010] In order that this invention may solve the above-mentioned technical problem, the need is

accepted in an organic pigment or carbon black. Namely, with a curing agent and a high molecular compound Anionic radical content organic high molecular compounds (it abbreviates to "anionic organic high molecular compounds" hereafter.) It is aquosity dispersion liquid containing the covered anionic microencapsulation pigment. The recording ink containing the anionic microencapsulation pigment content aquosity dispersion liquid for recording ink and these aquosity dispersion liquid which are characterized by being in the range the organic pigment in an anionic microencapsulation pigment or whose content of carbon black is 35 - 80 % of the weight is offered.

[0011] the recording ink containing the anionic microencapsulation pigment of this invention -- service water -- sex dispersion liquid The need is accepted in an organic pigment or carbon black. With a curing agent and a high molecular compound It covers with anionic organic high molecular compounds. Moreover, the content of the organic pigment or carbon black at 35 - 80 % of the weight Especially the thing whose mean particle diameter it is in the range whose mean particle diameter the maximum particle diameter of the primary particle of an organic pigment or carbon black is 200nm or less, and is 10-100nm, the maximum particle diameter of an anionic microencapsulation pigment is 1000nm or less, and is 300nm or less is desirable. Moreover, the thing of the form which neutralized anionic organic high molecular compounds by the base is desirable, and it is desirable to use especially alkali metal.

[0012] Furthermore, if the anionic microencapsulation pigment is the thing of the form which are the anionic organic high molecular compounds containing a curing agent and a high molecular compound, with covered the organic pigment, it is desirable much more.

[0013] Furthermore, other matter, such as a vehicle for titanium, the mineral matter like aluminum, a pigment derivative, a pigment agent, a pigment wetting agent, an organic solvent, a plasticizer, an ultraviolet ray absorbent, an anti-oxidant, or recording ink, can also be included into the capsule of the microencapsulation pigment of this invention again.

[0014]

[Embodiment of the Invention] As the manufacture approach of the anionic microencapsulation pigment contained in the aquosity dispersion liquid for recording ink of this invention, the two approaches of the physical and mechanical technique and the chemical technique, such as the coacervation method, interfacial polymerization, and the Inn SAICHU method, are mentioned as an approach from the former.

[0015] However, even if the particle size of the microencapsulation pigment obtained by these conventional-type approaches is the thing of the magnitude below submicron (micrometer) one, since particle diameter is large and the rate that the pigment in a microcapsule occupies is low, when recording ink is manufactured using this microencapsulation pigment, what can not necessarily be satisfied in the feeling of concentration of definition, color rendering properties, transparency, or a color is not obtained. Furthermore, it is necessary to manufacture a microencapsulation pigment with the rate for it to be detailed and high that the pigment in a microcapsule occupies.

[0016] Moreover, since the resin concentration in a capsule is high (pigment concentration is low), the ingredient used for recording ink is restricted, or in order to use a surfactant, a water resisting property is inferior.

[0017] As the manufacture approach of the anionic microencapsulation pigment contained in the aquosity dispersion liquid for recording ink of this invention Fundamentally a mixture (a composite or complex) with the anionic organic high molecular compounds which have self-dispersion power or dissolution ability to water, an organic pigment, or carbon black Or the approach of making a mixture with an organic pigment or carbon black, a curing agent, and an anionic organic high molecular compound an organic solvent phase, and throwing water into this organic solvent phase, or supplying this organic solvent phase underwater, and changing self-distribution (phase inversion emulsification) (it is hereafter called a "phase inversion method".) It is desirable.

[0018] It neutralizes that a basic compound is also in all the anionic all [ a part or ] of anionic radical content organic high molecular compounds. Or an organic pigment or carbon black, The water cake

obtained by the process which consists of a process kneaded in an aqueous medium, and a process which pH is carried out to an acid compound being at neutrality or acidity, and anionic radical content organic high molecular compounds are deposited, and fixes to a pigment. How to acquire by neutralizing all the anionic all [ a part or ] using a basic compound (it is hereafter called the "\*\*\*\* method".) It is desirable.

[0019] By doing in this way, the aqueous dispersion liquid containing the anionic microencapsulation pigment of a high pigment content more detailed than the conventional approach of making it into the purpose can be manufactured.

[0020] Moreover, in the describing [ above ] phase inversion method, even if it makes the vehicle and additive for recording ink mix into an organic solvent phase and manufactures, it is satisfactory in any way. If it says from the ability of the dispersion liquid for direct recording ink to be manufactured especially, will make it more more desirable to mix the vehicle for recording ink.

[0021] The maximum particle diameter is 200nm or less, and the organic pigment or carbon black contained in the microcapsule of an anionic microencapsulation pigment has desirable organic pigment or carbon black in the range whose mean particle diameter of a primary particle is 10-100nm, in order to acquire the feeling of concentration of recording ink, transparency, and color rendering properties, or in order to manufacture a detailed microencapsulation pigment with a mean particle diameter of 300nm or less.

[0022] Although especially the class of organic pigment used by this invention is not limited, if it limits for illustrating a typical thing The Quinacridone system pigment, the Quinacridone quinone system pigment, a dioxazine system pigment, Phthalocyanine pigment, an anthra pyrimidine system pigment, an anthanthrone pigment, An indan SURON system pigment, a flavan SURON system pigment, a perylene system pigment, a diketopyrrolopyrrole pigment, A peri non system pigment, a kino FUTARON system pigment, an anthraquinone system pigment, a thioindigo system pigment, a Benz imidazolone system pigment, an isoindolinone system pigment, an azomethine system pigment, or azo pigment is mentioned.

[0023] Moreover, as for carbon black, neutrality, acidity, basic carbon, etc. are mentioned.

[0024] As a curing agent which may be contained with the pigment in the microcapsule of an anionic microencapsulation pigment For example, amino resin, such as melamine resin, benzoguanamine resin, and a urea-resin, Phenol resin, such as a TORIMECHI roll phenol and its condensate, tetramethylene di-isocyanate (TDI), Diphenylmethane diisocyanate (MDI), hexamethylene di-isocyanate (HDI), Naphthalene diisocyanate (NDI), isophorone diisocyanate (IPDI), The poly isocyanates, such as xylylene diisocyanate (XDI), those denaturation isocyanates, and blocked isocyanate, Fatty amine, aromatic amine, N-methyl piperazine, triethanolamine, Amines, such as a morpholine, dialkylamino ethanol, and benzyl dimethylamine, Polycarboxylic acid, phthalic anhydride, a maleic anhydride, anhydrous hexahydrophthalic acid, Acid anhydrides, such as pyromellitic dianhydride, anhydrous benzophenone tetracarboxylic acid, and ethylene glycol bis(trimellitate), The bisphenol A mold epoxy resin, a phenol system epoxy resin, a glycidyl methacrylate copolymer, Epoxy compounds, such as glycidyl ester resin of a carboxylic acid, and alicyclic epoxy, Polyether polyol, a polybutadiene glycol, the poly caprolactone polyol, Alcohols, such as tris hydroxyethyl isocyanate (THEIC), Vinyl compounds, such as a polyvinyl compound as a partial saturation radical content compound used for radical hardening or UV hardening by peroxide, or electron ray hardening, the Pori allyl compound, a glycol, and a reactant of polyol, an acrylic acid, or a methacrylic acid, etc. are mentioned.

[0025] As for these curing agents, it is more desirable to be used in order to harden the wall of an anionic microencapsulation pigment, or in order to raise the paint film reinforcement at the time of using it for recording ink, to add a photoinitiator, a polymerization initiator, or a catalyst, if still more nearly required, and to aim at promotion of hardening.

[0026] As a photoinitiator used for such the purpose, although benzoin, anthraquinone,

benzophenones, \*\* sulfur compounds, dimethylbenzyl ketal, etc. are mentioned, it is not the object limited to these.

[0027] Similarly, as a polymerization initiator, \*\*\*\* azo compounds, such as \*\*\*\* peroxide; azobis isobutyl nitril, such as t-butyl peroxybenzoate, G t-butyl peroxide, cumene par hydroxide, acetyl peroxide, benzoyl peroxide, and lauroyl peroxide, azobis-2,4-dimethylvaleronitrile, and azobis cyclohexane carbonitrile, etc. are mentioned, for example.

[0028] Moreover, as a catalyst, Co compound, Pb compound, etc. are mentioned similarly, for example.

[0029] Although the high molecular compound which may be contained with the pigment in the microcapsule of an anionic microencapsulation pigment can be especially used without a limit if it is a with a number average molecular weight of 1,000 or more thing, the field of the film reinforcement of recording ink and the manufacture side of a capsule to its number average molecular weight is [ the thing of the range of 3,000-100,000 ] desirable.

[0030] Although especially the class of such a high molecular compound is not limited, for example A vinyl chloride, Polyvinyl systems, such as vinyl acetate, polyvinyl alcohol, and a polyvinyl butyral, Polyester systems, such as alkyd resin and phthalic resin, melamine resin, melamine formaldehyde resin, Amino systems, such as amino alkyd copolycondensation resin, a urea resin, and a urea-resin, thermoplasticity, High molecular compounds, such as the acrylic of thermosetting or denaturation, an epoxy system, a polyurethane system, a polyether system, a polyamide system, an unsaturated polyester system, a phenol system, a silicone system, and a fluorine system, those copolymers, or mixture is mentioned.

[0031] The anionic organic high molecular compounds used in order to manufacture an anionic microencapsulation pigment Although it has self-dispersion power or dissolution ability to water, and there will be no limit especially if it is anionic (acidity), in order to obtain what becomes enough as the capsule film or a paint film of recording ink Usually, the thing of the range of 1,000-100,000 has desirable number average molecular weight, and especially the thing of the range of 3,000-50,000 is desirable, and what dissolves in an organic solvent and serves as a solution is desirable.

[0032] Especially the self-dispersion power or dissolution ability of anionic organic high-molecular-compounds itself is given by neutralizing the anionic radical like the carboxyl group in the anionic organic high molecular compound concerned, a sulfonic acid group, or a phosphonic acid radical using alkali metal, such as ammonia, an organic amine like triethylamine, a sodium hydroxide and a potassium hydroxide, and a lithium hydroxide, for example, although not limited. Especially desirable self-dispersion power or dissolution ability is the thing of the form of making a carboxyl group introduce into these organic high molecular compounds, and being a base, with making it neutralize. In anionic organic high molecular compounds, you may have two or more sorts of these anionic radicals.

[0033] 30 or more KOHmg/g has the desirable acid number, and the amount of the carboxyl group in the anionic high molecular compounds which have a carboxyl group has the more desirable range used as 50-250. If the acid number of anionic high molecular compounds exceeds 250, since it is in the inclination for the storage stability of a capsule to be spoiled or for the water resisting property of a record image to fall remarkably, and a hydrophilic property will become high too much and it is in the inclination for the stability of a capsule to be spoiled or for particle diameter to become large when the acid number is lower than 30, it is not desirable.

[0034] As such anionic organic high molecular compounds For example, polyvinyl systems, such as a vinyl chloride, vinyl acetate, polyvinyl alcohol, and a polyvinyl butyral, Polyester systems, such as alkyd resin and phthalic resin, melamine resin, melamine formaldehyde resin, The ingredient of amino systems, such as amino alkyd copolycondensation resin, a urea resin, and a urea-resin; Thermoplasticity, The acrylic of thermosetting or denaturation, an epoxy system, a polyurethane system, The ingredient which has anionic radicals, such as a polyether system, a polyamide system, an unsaturated polyester system, a phenol system, a silicone system, fluorine system high molecular



compounds, those copolymers, or mixture, is mentioned.

[0035] The anionic organic high molecular compounds used by this invention Although it has the molecular weight which becomes enough as a capsule wallplate and actuation especially of the formation of wall formation is not needed, in order to make properties, such as the solvent resistance of a capsule wall, and endurance, improvement-ize further In order to raise the film reinforcement after film formation of recording ink, to or anionic organic high-molecular-compounds itself which is used beforehand By carrying out the pendant of the reactant active group like glycidyl group, isocyanate radical, hydroxyl-group or alpha, and beta-ethylene nature partial saturation double bond (vinyl group) Or by making photo-curing agents, such as the cross linking agent which has a reactant active group, for example, melamine resin, a urethane resin epoxy resin, an ethylene nature partial saturation monomer, and oligomer, etc. mix These reactant active groups, functional groups, etc. are used the time of formation of a capsule, or after formation or paint film formation of recording ink. It is more desirable to make the engine performance which is made to increase-ize, or constructs a bridge and gels the molecular weight of anionic organic high-molecular-compounds itself as an object for capsule wallplates give.

[0036] Among anionic organic high molecular compounds, further, anionic acrylic resin carries out the polymerization of these monomers and other monomers which may be copolymerized in a solvent to the acrylic monomer (it abbreviates to an anion radical content acrylic monomer hereafter) which has for example, an anionic radical, and is obtained with it if needed. Especially the acrylic monomer that the acrylic monomer which \*\* one or more anionic radicals chosen from the group which consists of a carboxyl group, a sulfonic group, and a HOSUHON radical as an anion radical content acrylic monomer, for example is mentioned, and has a carboxyl group also in these is desirable.

[0037] As an acrylic monomer which has a carboxy kill radical, an acrylic acid, a methacrylic acid, a crotonic acid, ethacrylic acid, a propyl acrylic acid, an isopropyl acrylic acid, an itaconic acid, boletic acid, etc. are mentioned, for example. An acrylic acid and a methacrylic acid are desirable also in these.

[0038] As an acrylic monomer which has a sulfonic group, sulfoethyl methacrylate, a butyl acrylamide sulfonic acid, etc. are mentioned, for example.

[0039] As an acrylic monomer which has a HOSUHON radical, phospho ethyl methacrylate etc. is mentioned, for example.

[0040] As an anion radical content acrylic monomer and other monomers which may be copolymerized For example, a methyl acrylate, an ethyl acrylate, acrylic-acid isopropyl, Acrylic-acid-n-propyl, acrylic-acid-n-butyl, acrylic-acid-t-butyl, 2-ethylhexyl acrylate, acrylic-acid-n-octyl, acrylic-acid lauryl, Acrylic-acid benzyl, a methyl methacrylate, ethyl methacrylate, methacrylic-acid isopropyl, Methacrylic-acid-n-propyl, n-butyl methacrylate, methacrylic-acid isobutyl, T-butyl methacrylate, 2-ethylhexyl methacrylate, n-octyl methacrylate, Methacrylic-acid lauryl, stearyl methacrylate, tridecyl methacrylate, \*\*\*\* (meta) acrylic ester [, such as methacrylic-acid benzyl, ]; -- addition reaction object [ of stearin acid, \*\*\*\*\* fatty acids, such as an addition reaction object of glycidyl methacrylate, and the acrylic ester monomer that has oxirane structure (meta) ]; -- a three or more carbon atomic numbers alkyl group The addition reaction object of the oxirane compound and acrylic acid (meta) which are included; Styrene, Alpha methyl styrene, o-methyl styrene, m-methyl styrene, p-methyl styrene, \*\*\*\* styrene system monomer [, such as p-tert-butyl styrene, ]; -- \*\*\*\* itaconic-acid ester [, such as itaconic-acid benzyl, ]; -- \*\*\*\* maleates [, such as maleic-acid dimethyl, ]; -- \*\*\*\* boletic acid ester [, such as boletic acid dimethyl, ]; -- acrylonitrile and a methacrylonitrile -- Vinyl acetate, acrylic-acid isobornyl, methacrylic-acid isobornyl, Acrylic-acid aminoethyl, acrylic-acid aminopropyl, methyl-acrylate aminoethyl, Acrylic-acid methylaminopropyl, ethyl-acrylate aminoethyl, Acrylic-acid ethylaminopropyl, an acrylic-acid aminoethyl amide, An acrylic-acid aminopropyl amide, a methyl-acrylate aminoethyl amide, An acrylic-acid methylaminopropyl amide, an ethyl-acrylate aminoethyl amide, An acrylic-acid ethylaminopropyl amide, a methacrylic-acid amide, methacrylic-acid aminoethyl, Methacrylic-acid aminopropyl,

methyl-methacrylate aminoethyl, methacrylic-acid methylaminopropyl, Ethyl methacrylate aminoethyl, methacrylic-acid ethylaminopropyl, A methacrylic-acid aminoethyl amide, a methacrylic-acid aminopropyl amide, A methyl-methacrylate aminoethyl amide, a methacrylic-acid methylaminopropyl amide, An ethyl methacrylate aminoethyl amide, a methacrylic-acid ethylaminopropyl amide, Acrylic-acid hydroxymethyl, acrylic-acid-2-hydroxyethyl, 2-hydroxypropyl acrylate, methacrylic-acid hydroxymethyl, methacrylic-acid-2-hydroxyethyl, 2-hydroxypropyl methacrylate, N-methylol acrylamide, allyl alcohol, etc. are mentioned.

[0041] As a monomer which has a cross-linking functional group, it is listed below.

[0042] The polymerization nature monomer which has a block isocyanate radical can be easily manufactured carrying out the addition reaction of the well-known block agent to the polymerization nature monomer which has isocyanate radicals, such as 2-methacryloiloxy-ethyl isocyanate, or by carrying out the addition reaction of the compound which has an isocyanate radical and a block isocyanate radical to the vinyl system copolymer which has the hydroxyl group and carboxyl group which were mentioned above. The compound which has an isocyanate radical and a block isocyanate radical can be easily obtained by carrying out the addition reaction of as well-known the block agent as a diisocyanate compound at about 1:1 rate by the mole ratio.

[0043] As a monomer which has an epoxy group, the acrylate monomer which has glycidyl (meta) acrylate and an alicyclic epoxy group (meta) is mentioned, for example.

[0044] As a monomer which has a 1 and 3-dioxolane-2-ON-4-IRU radical, 1, 3-dioxolane-2-ON-4-ylmethyl (meta) acrylate, 1, and 3-dioxolane-2-ON-4-ylmethyl vinyl ether etc. is mentioned, for example.

[0045] As a polymerization initiator, \*\*\*\* azo compounds, such as \*\*\*\* peroxide; azobis isobutyl nitril, such as t-butyl peroxybenzoate, G t-butyl peroxide, cumene par hydroxide, acetyl peroxide, benzoyl peroxide, and lauroyl peroxide, azobis-2,4-dimethylvaleronitrile, and azobis cyclohexane carbonitrile, etc. are mentioned, for example.

[0046] With an anionic radical content acrylic monomer, further as a solvent used in case the polymerization of other monomers which may be copolymerized with these monomers if needed is carried out For example, \*\*\*\* aliphatic hydrocarbons, such as a hexane and a mineral spirit; Benzene, \*\*\*\* ester solvents [, such as \*\*\*\* aromatic-hydrocarbons-solvent; butyl acetate ], such as toluene and a xylene; A methyl ethyl ketone, \*\*\*\* ketones, such as isobutyl methyl ketone; A methanol, ethanol, \*\*\*\* alcohols solvents, such as a butanol and isopropyl alcohol; \*\*\*\* aprotic polar solvents, such as dimethylformamide, dimethyl sulfoxide, N-methyl pyrrolidone, and a pyridine, etc. are mentioned. These solvents can also use together and use two or more sorts.

[0047] The anionic microencapsulation pigment content aquosity dispersion liquid by the phase inversion method are the following, and are made and manufactured.

[0048] The anionic organic high molecular compounds which have self-dispersion power or dissolution ability to water in a phase inversion method, an organic pigment, or a mixture with carbon black (a composite or complex), Or although anything can be used as long as especially the organic solvent used in case a mixture with an organic pigment or carbon black, a curing agent, and an anionic organic high molecular compound is made into an organic solvent phase is not limited and may dissolve anionic organic high molecular compounds The alcohols solvent like the acetone from the field of the ease of the solvent removal at the time of manufacture, the ester solvent; ethanol like the ketones; ethyl acetate like a methyl ethyl ketone, and isopropyl alcohol; the solvent of the low-boiling point of the aromatic hydrocarbons solvent like benzene etc. is desirable.

[0049] The rate of anionic organic high molecular compounds has the desirable range of the 25 - 186 weight section to the 100 weight sections of an organic pigment or carbon black, and especially its range of the 30 - 150 weight section is desirable.

[0050] Although I hear that the cross linking agent and the high molecular compound are dissolving into

anionic organic high molecular compounds and it has them that it is especially desirable for the mixture (a composite or complex) which is an organic phase, without a pigment condensing in any way minutely in organic high molecular compounds at homogeneity while distributed stabilization is carried out, it is never limited only to this.

[0051] Although not limited, if it limits especially as a distributed stabilization process of this mixture for illustrating only what [ those ] are especially typical also by striking (1) A powder organic pigment or carbon black is made to micro-disperse-ize in anionic organic high molecular compounds using various dispersers, such as a bead mill, a roll mill, and a sand mill. Subsequently The approach that a curing agent, a high molecular compound, etc. are said that you make it dissolve or decentralize, Or the sentiment cake after composition of (2) organic pigments or the wet cake of carbon black, The thing of a condition [ having made water decentralize a pigment freely ] is made to micro-disperse-ize by used and carrying out Flushing of the various dispersers, such as a kneader, into the anionic organic high molecular compounds before neutralization. Namely, subsequently The approach that a curing agent, a high molecular compound, etc. are said that you make it dissolve or decentralize etc. is mentioned. In these distributed approaches, in order to obtain an ultrafine particle, bead mill distribution or the approach of carrying out Flushing is more desirable.

[0052] Moreover, since a sentiment cake is used, the desiccation process of organic pigments is not needed, it becomes energy saving and the firm condensation which takes place into a desiccation process moreover does not take place at all, either, the usefulness of especially the latter approach is very high.

[0053] Furthermore, the pigment derivative which has a dialkyl aminomethyl radical, a SUFONSAN radical, a SUFON amide group, a phthalimide radical, etc. for the purpose of distributed stabilization; pigment agents, such as the "Sol Spurs 24000" etc. by "BYK-160" made from big KEMI, "BYK-166", and Zeneka Co., etc. can be used, and distributed time amount etc. can also be shortened.

[0054] in order to make self-distribution (phase inversion emulsification) easy, and in order to make solvent removal actuation simple -- mixing -- as for the amount of the solvent used in the living body, stopping as low as possible is desirable, and, as for the viscosity of such a field to these mixtures, preparing to 10000 or less CPs is desirable.

[0055] Although self-distribution (phase inversion emulsification) is carried out throwing water into the organic phase of a mixture, or by supplying this organic phase underwater, as the approach, the microencapsulation pigment made into the purpose can be formed by supplying another side slowly into it in an instant, agitating either an organic phase or water moderately.

[0056] Since a class, a rate, etc. of an agitator in such churning seldom affect the magnitude of the particle formed, especially the class or agitating speed of an agitator are not restricted.

[0057] In such a process, although it is possible for the thing of the above-mentioned procedure to also make a sufficiently detailed microencapsulation pigment, as an approach of making a still more detailed thing, it is carrying out phase inversion emulsification, hitting a supersonic wave to an organic phase. Although especially the frequency of the supersonic wave is not limited, it is 10-200kHz preferably.

[0058] In case the so-called neutralization type of anionic organic high molecular compounds are used, only an initial complement needs to make the bases for neutralization dissolve in an organic phase or the aqueous phase beforehand. It is more desirable to dissolve bases in the aqueous phase in consideration of condensation of the pigment in an organic phase especially.

[0059] Moreover, even if the cross linking agent used in order to carry out gelation processing of the formed capsule wall, or in order to raise the film reinforcement after film formation of recording ink is the case where the compound of \*\*\*\* water solubility of for example, polyamine is used, it needs to dissolve only an initial complement in an organic phase beforehand.

[0060] According to the gestalt with which practical use is presented, the anionic microencapsulation pigment content aquosity dispersion liquid obtained by these various approaches can also be used as it

is, or they can perform desolventization and it can also be used for them as an aqueous dispersing element.

[0061] General distillation, a vacuum distillation method, etc. are mentioned as an approach of performing desolventization.

[0062] The method (the \*\*\*\* method) of obtaining anionic microencapsulation pigment content aqueous dispersion liquid is based on the following procedures by, using the same ingredient as the above on the other hand, and neutralizing all the anionic all [ a part or ] for the water cake which consists of anionic radical content organic high molecular compounds and an organic pigment, or carbon black using a basic compound.

(1) Distribute anionic organic high molecular compounds and a pigment in an alkaline aqueous medium. Moreover, it heat-treats if needed and gelation of resin is attained.

(2) By making pH into neutrality or acidity, carry out hydrophobing of the resin and fix resin to a pigment strongly.

(4) Perform filtration and rinsing if needed.

(5) Neutralize a carboxyl group as a basic compound is also, and re-distribute in an aqueous medium. Moreover, it heat-treats if needed and gelation of resin is attained.

[0063] As an approach of distributing the anionic organic high molecular compounds and pigment in a process (1) in an alkaline aqueous medium, the two following approaches are suitable.

(1) Distribute in an aqueous medium after kneading a pigment in an organic solvent medium.

(2) Mix or knead a pigment in an aqueous medium.

[0064] By the approach of \*\*\*\*\* (1), a pigment and the organic solvent solution of anionic organic high molecular compounds are first distributed minutely using well-known dispersers, such as a ball mill, a sand mill, and a colloid mill.

[0065] Although all the things for which the organic solvent used is generally used at this time can be used, the solubility over resin is good, the thing and vapor pressure in which the composition top of resin does not have a problem, either are higher than water, and what is easy to carry out desolventization, and a thing with water and a miscibility are still more desirable. As such a solvent, an acetone, a methyl ethyl ketone, a methanol, ethanol, n-propanol, isopropanol, ethyl acetate, a tetrahydrofuran, etc. are mentioned, for example. Although the miscibility with water is low, methyl isopropyl ketone, a methyl-n-propyl ketone, isopropyl acetate, n-propyl acetate, a methylene chloride, benzene, etc. can be used for this approach.

[0066] In order to distribute the dispersing element which consists of the pigment and anionic organic high molecular compounds which were distributed in the organic solvent medium in an aqueous medium

(1) The approach which neutralizes the carboxyl group of anionic organic high molecular compounds using a basic compound, hydrophilic-property-izes anionic organic high molecular compounds, and water is made to distribute, Or the method of making water distribute the dispersing element which consists of the anionic organic high molecular compounds and pigment which were neutralized using (2) basicity compounds is mentioned.

[0067] As the distributed approach to water, the following approaches are suitable.

(a) Water is dropped after neutralizing the dispersing element which consists of anionic organic high molecular compounds and a pigment using a basic compound.

(b) Water is dropped at the dispersing element which consists of the anionic organic high molecular compounds and pigment which were neutralized using the basic compound.

(c) The water containing a basic compound is dropped at the dispersing element which consists of anionic organic high molecular compounds and a pigment.

(d) Neutralize that a basic compound is also about the dispersing element which consists of anionic organic high molecular compounds and a pigment, and add in a water medium.

(e) Add the dispersing element which consists of the anionic organic high molecular compounds and

pigment which were neutralized using the basic compound in an aqueous medium.

(f) Add the dispersing element which consists of anionic organic high molecular compounds and a pigment in the water medium containing a basic compound.

[0068] When distributing in water, you may carry out using high SHIEA churning with churning by usual low SHIEA, a homogenizer, etc., or a supersonic wave. Moreover, a surfactant, protective colloid, etc. can also be used together in the range in which the water resisting property of a paint film is not remarkably reduced as the purpose which assists the distribution to an aqueous medium is also.

[0069] As a basic compound, a sodium hydroxide, a potassium hydroxide, the alkali-metal; ammonia like a lithium hydroxide, triethylamine, tributylamine, dimethylethanolamine, diisopropanolamine, the organic amine like a morpholine, etc. are mentioned, for example.

[0070] It neutralizes first using the basic compound which described above the carboxyl group of anionic organic high molecular compounds, and the approach of kneading resin and a pigment in the aqueous medium which is the approach of \*\* (2) which can apply anionic organic high molecular compounds and a pigment to the \*\* (1) process distributed in an alkaline aqueous medium is mixed or kneaded with a pigment in an aqueous medium. At this time, even if the resin dissolved or distributed in water contains the organic solvent, it may not interfere, it may perform desolventization, and may be the medium of only water substantially. Both a powdered pigment an aqueous slurry and a filter press cake can be used for a pigment. When distributing in an aqueous medium, in order to simplify a production process, as for a pigment, it is desirable to use few aqueous slurries or filter press cakes of secondary condensation of a pigment particle. The same approach as the case of distribution in an organic solvent medium and the same ingredient of the kneading approach, an organic solvent, and a basic compound are usable.

[0071] an organic solvent system and an aqueous system – even if it is the case of which kneading, a pigment agent and a wetting agent can also be used in the range in which the water resisting property of a record image is not reduced for the purpose which assists distribution of a pigment.

[0072] Moreover, before \*\*\*\*(ing) by being after kneading in case a pigment is kneaded or, the curing catalyst of matter other than a pigment, for example, a color, an anti-oxidant, an ultraviolet ray absorbent, and a coating binder, a rust-proofer, perfume, drugs, etc. can also be added.

[0073] the operating rate of anionic organic high molecular compounds – the 100 weight sections of an organic pigment -- receiving -- the 25 - 186 weight section -- desirable -- 30 to 150 weight -- the section -- within the limits is suitable. Since it is in the inclination whose allowances on the design of mix are lost when there are few operating rates of anionic organic high molecular compounds than 25 weight sections, it was in the inclination which stops being able to distribute a pigment easily sufficiently minutely, and the rate of the pigment in a dispersing element decreases when [ than the 186 weight sections ] more and a watercolor pigment dispersing element is used for recording ink, it is not desirable.

[0074] Furthermore, when attaining gelation of anionic organic high molecular compounds by heat-treatment after kneading a pigment, it is desirable to perform the nonvolatile matter of the dispersion liquid after kneading at 10% or less preferably 15% or less.

[0075] Moreover, although it will be satisfactory in any way if whenever [ stoving temperature ] is beyond temperature to which bridge formation of resin progresses, a desirable temperature requirement is 70 degrees C - 200 degrees C. Since whenever [ stoving temperature ] is in the inclination which crystal growth is carried out depending on the class of pigment, or distributed stability breaks, and is hard to encapsulate when bridge formation time amount is taken too much and whenever [ stoving temperature ] exceeds 200 degrees C at less than 70 degrees C, it is not desirable.

[0076] \*\*\*\* performed in order to fixing-ize resin strongly to the pigment by which micro-disperse was carried out into the aqueous medium hydrophobicity-izes resin by adding an acid compound for the carboxyl group of the anionic organic high molecular compounds neutralized with the basic compound, and making pH into neutrality or acidity.

[0077] As an acid compound used, although the organic acids like a hydrochloric acid, a sulfuric acid,

phosphoric acid, the inorganic-acids; formic acid like a nitric acid, an acetic acid, and a propionic acid can be used for example, the hydrochloric acid or sulfuric acid also with the large \*\*\*\* effectiveness with little [ and ] organic substance is desirable. [ under wastewater ] Although pH at the time of \*\*\*\* has the desirable range of 2-6, there are some which are decomposed with an acid depending on a pigment, and, in the case of such a pigment, it is desirable to \*\*\*\* in the range of pH 4-7. Before performing \*\*\*\*, it is desirable to remove beforehand the organic solvent which exists in a system using approaches, such as vacuum distillation.

[0078] Filtration and rinsing are performed after \*\*\*\* if needed, and the water cake of a distributed pigment is obtained. As the filtration approach, well-known approaches, such as suction filtration, pressure filtration, and centrifugal separation, are employable.

[0079] This water cake is re-distributed in an aqueous medium, holding a detailed condition without a pigment particle condensing by re-neutralizing a carboxyl group, without making it dry, as a basic compound is also with the condition of having carried out water. Concomitant use with independence, such as an organic amine compound which can volatilize [ diethanolamine / alkali metal, such as a sodium hydroxide, a potassium hydroxide, and a lithium hydroxide, nor / neither / triethanolamine, diethanolamine ] easily in consideration of redispersible and the water resisting property of recording ink as a basic compound, or these, and the volatile amine compound like ammonia, triethylamine, and dimethylethanolamine is desirable.

[0080] Thus, without the so-called auxiliary materials, such as an emulsifier, capsulation of a minute particle is possible also for \*\*, and the anionic microencapsulation pigment used by this invention can be made very simple, and can prepare a minute capsule in any way.

[0081] The actual measurement which added and averaged the major axis and minor axis of a pigment of dozens samples is used for the mean particle diameter of the organic pigment in the microencapsulation pigment used by this invention using the photograph taken with the electron microscope.

[0082] The mean particle diameter of the microencapsulation pigment used by this invention can also be measured using the particle diameter measuring device of a laser-doppler method, although it is desirable to use the actual measurement measured with the electron microscope since a some difference comes out with a particle diameter measuring method.

[0083] Thus, the distributed stability of a pigment is improved more than before, and the anionic microencapsulation pigment content aqueous dispersion liquid obtained have the advantage that engine performance, such as definition of recording ink, lightfastness, color rendering properties, and transparency, improves, by using it as a color material of recording ink. Moreover, since the pigment concentration in a microcapsule is high, versatility is high, and since laborsaving of the process which distributes a pigment can be performed, there is also an advantage that laborsaving of distributed energy and an effort can be attained. Moreover, in order not to use a surfactant etc., a water resisting property also improves. Furthermore, since the oily curing agent and the oily vehicle for recording ink which were not able to be used conventionally can be included in the capsule of a microencapsulation pigment, the width of face of the ingredient which can be used can also manufacture breadth and direct recording ink.

[0084] As claim 1 prescribed, the content of the organic pigment in an anionic microencapsulation pigment has 35 - 80% of the weight of the desirable range. Since the resin concentration in a capsule becomes high when there is less content of the organic pigment in an anionic microencapsulation pigment than 35% Since versatility is missing since an additive and compatibility, such as resin for recording ink, and a solvent, an assistant, may be restricted or the addition of the additive etc. is restricted, and the pigment concentration in a capsule becomes low further, As a result of making high the operating rate of the microencapsulation pigment in recording ink in order not to raise the depth of shade or to raise the depth of shade when it is used as aqueous dispersion liquid as recording ink, since

it is in the inclination for the viscosity of recording ink to become high, it is not desirable. Moreover, when there is more content of the organic pigment in an anionic microencapsulation pigment than 80 % of the weight, since it is in the inclination which stops being able to distribute an organic pigment easily minutely, it is not desirable.

[0085] Moreover, since blinding of the nozzle of a jet ink printer is carried out when the maximum particle diameter of an anionic microencapsulation pigment becomes larger than 1000nm, as claim 2 prescribed, the maximum particle diameter of an anionic microencapsulation pigment is 1000nm or less, and what is 500nm or less is more desirable [ the particle diameter ].

[0086] Furthermore, the mean particle diameter of the organic pigment in the anionic microencapsulation pigment has desirable 300nm or less, and especially its 250nm or less is desirable. the case where it is used as recording ink since it will sediment, or it will be encapsulated after the pigment has condensed on the occasion of microencapsulation when the microencapsulation pigment in dispersion liquid saves at a long period of time if the mean particle diameter of the organic pigment to be used becomes larger than 300nm -- color enhancement -- transparent -- it is -- when definition is inferior and you record on an OHP sheet etc. especially, transparency of light interrupts and a beautiful color projects -- since it is in the inclination which is not, it is not desirable .

[0087] As for the anionic organic high molecular compounds in the anionic microencapsulation pigment of this invention, it is desirable to be used in the form of the salt of alkali metal or an organic amine. Although it is in the inclination for the water resisting property of the record image to worsen since an inorganic base remains in a record image when it is used in the form of the salt of alkali metal, such as a sodium hydroxide, a potassium hydroxide, and a lithium hydroxide, it is desirable from excelling in redispersible and the dependability of recording ink becoming high.

[0088] As the above-mentioned organic amine, organic amines of a high-boiling point which cannot volatilize easily, such as ammonia, triethylamine, tributylamine, dimethylethanolamine, diisopropanolamine, volatile amine compound; diethanolamine like a morpholine, and triethanolamine, are mentioned, for example.

[0089] Below 70 weight sections of the content of the anionic microencapsulation pigment contained in the anionic microencapsulation pigment content aqueous dispersion liquid for recording ink of this invention are desirable in the aqueous dispersion-liquid 100 weight section, its range of 2 - 60 weight section is more desirable to it, and especially its range of 10 - 50 weight section is desirable to it. Since condensation of a microcapsule takes place since it is in the inclination for aqueous dispersion liquid to present the shape of a solid substantially when the content of the microencapsulation pigment in aqueous dispersion liquid becomes higher than 70 weight sections, and distribution is needed again, it is not desirable. moreover, when the content of the microencapsulation pigment in aqueous dispersion liquid became less than 2 weight sections and it is used for recording ink, since it is in the inclination which does not profit have the enough depth of shade, it is not desirable. Considering adding the additive for raising the engine performance to recording ink, when there are few contents of the microencapsulation pigment in aqueous dispersion liquid than 10 weight sections, since it is in the inclination for the addition of an additive to be restricted, it is not desirable.

[0090] The recording ink containing the aqueous dispersion liquid containing the anionic microencapsulation pigment of this invention mixes the anionic microencapsulation pigment content aqueous dispersion liquid and the water-soluble organic solvent which were explained above, water, etc., and is prepared. Furthermore, water soluble resin, an organic amine, a surfactant, antiseptics, a viscosity controlling agent, pH regulator, a chelating agent, etc. can also be added if needed.

[0091] When the saturation of the depth of shade as recording ink, definition, transparency, and a hue etc. is taken into consideration, the content rate of the anionic microencapsulation pigment content aqueous dispersion liquid in the recording ink of this invention has 1 - 100% of the weight of the desirable range, and 5 - 100% of the weight of especially its range is desirable. Considering offering recording ink



directly especially, it cannot be overemphasized that 100 % of the weight is desirable.

[0092] As a water-soluble organic solvent used for recording ink, for example Methyl alcohol, Ethyl alcohol, n-butyl alcohol, isobutyl alcohol, Alcohols, such as tert-butyl alcohol, n-propyl alcohol, and isopropyl alcohol; Dimethyl formaldehyde, Amides, such as dimethylacetamide; Ketones; tetrahydrofurans, such as an acetone and a methyl ethyl ketone, Dioxane, ethylene glycol methyl ether, ethylene glycol ethyl ether, Diethylene-glycol methyl ether, diethylene-glycol ethyl ether, Ether, such as the triethylene glycol monomethyl ether and TORIECHIREN ethylene glycol monoethyl ether, Ethylene glycol, Propylene glycol, a butylene glycol, triethylene glycol, Polyhydric-alcohol; N-methyl-pyrrolidones, such as 1, 2, 6-hexane triol, thiodiglycol, a diethylene glycol, a polyethylene glycol, a polypropylene glycol, and a glycerol, 1,3-dimethyl-2-imidazolidinone, etc. are mentioned. Also in these water-soluble organic solvents, polyhydric alcohol and ether are desirable.

[0093] The content rate of the water-soluble organic solvent in recording ink has 95 or less desirable % of the weight, and 0 - 80% of the weight of especially its range is desirable.

[0094] As water soluble resin used for recording ink if needed, synthetic macromolecules, such as natural protein, such as glue, gelatin, casein, albumin, gum arabic, and fish GURYU, an alginic acid, methyl cellulose, a carboxymethyl cellulose, polyethylene oxide, hydroxyethyl cellulose, polyvinyl alcohol, polyacrylamide, aromatic amide, polyacrylic acid, polyvinyl ether, a polyvinyl pyrrolidone, an acrylic, and polyester, etc. are mentioned, for example.

[0095] Water soluble resin is the purpose which mentions fixable, and quick-drying [ viscosity accommodation and quick-drying ], the content rate of the water soluble resin in the recording ink in the case of being used if needed and using it for recording ink has 30 or less desirable % of the weight, and especially its 20 or less % of the weight is desirable.

[0096] As an organic amine used for recording ink if needed, ethanolamine, diethanolamine, triethanolamine, N-methylethanol amine, N-ethyl diethanolamine, 2-amino-2-methyl propanol, 2-ethyl-2-amino-1,3-propanediol, 2-(aminoethyl) ethanolamine, tris (hydroxymethyl) aminomethane, ammonia, a piperidine, morpholine, etc. are mentioned, for example.

[0097] The manufacture approach of the recording ink of this invention does not need at all a disperser which distributes a pigment, but it is easy agitators, such as DISUPA, and, but only the actuation which carries out churning mixing can manufacture anionic microencapsulation pigment content aqueous dispersion liquid, a water-soluble organic solvent, water, water soluble resin, etc. Moreover, a surfactant, antiseptics, a viscosity controlling agent, pH regulator, a chelating agent, etc. are added and manufactured if needed at the time of churning.

[0098] thus, the manufactured recording ink – \*\*\*\* for image recording, such as a jet printer, – it excels in redispersible [ of a record image / the definition the color enhancement, the transparency, the water resisting property or redispersible ] by things, and sharp reduction of the manufacturing cost of recording ink can be aimed at by laborsaving of a distributed process.

## EXAMPLE

[Example] Hereafter, this invention is further explained to a detail using an example and the example of a comparison. Below, especially the "section" and "%", as long as there is no notice, the "weight section" and "% of the weight" are expressed.

[0100] <The synthetic example 1> (composition of anionic radical content organic high molecular compounds)

The mixed liquor which consists of the n-butyl methacrylate 175 section, the n-butyl acrylate 10.7 section, the beta-hydroxyethyl methacrylate 37.5 section, the methacrylic-acid 26.8 section, and the "par butyl O" (tert-butylperoxy octoate by Nippon Oil & Fats Co., Ltd.) 5.0 section was prepared.

[0101] Next, after carrying out a temperature up to 75 degrees C, agitating under a N2 seal after teaching the methyl-ethyl-ketone 250 section to a flask, the above-mentioned mixed liquor was dropped for 2 hours, it was made to react at this temperature further for 15 hours, and the acid number of solid content obtained the solution of 70 and the vinyl system resin of number average molecular weight 12500. The nonvolatile matter of this resin solution was 48%. Hereafter, this is written as a resin solution (A-1).

[0102] <The synthetic example 2> (composition of anionic radical content organic high molecular compounds)

The mixed liquor which consists of the styrene 43 section, the n-butyl acrylate 87.5 section, the beta-hydroxyethyl methacrylate 37.5 section, the methacrylic-acid 19.5 section, and the "par butyl O"5.0 section was prepared.

[0103] Next, after carrying out a temperature up to 75 degrees C, agitating under a N2 seal after teaching the methyl-ethyl-ketone 250 section to a flask, the above-mentioned mixed liquor was dropped for 2 hours, it was made to react at this temperature further for 15 hours, and the acid number of solid content obtained the solution of 48 and the vinyl system resin of number average molecular weight 14000. The nonvolatile matter of this resin solution was 49%. Hereafter, this is written as a resin solution (A-2).

[0104] <The synthetic example 3> (composition of anionic radical content organic high molecular compounds)

The mixed liquor which consists of the styrene 100 section, the n-butyl acrylate 40.3 section, the beta-hydroxyethyl methacrylate 37.5 section, the methacrylic-acid 9.7 section, and the "par butyl O"5.0 section was prepared.

[0105] Next, after carrying out a temperature up to 75 degrees C, agitating under a N2 seal after teaching the methyl-ethyl-ketone 250 section to a flask, the above-mentioned mixed liquor was dropped for 2 hours, it was made to react at this temperature further for 15 hours, and the acid number of solid content obtained the solution of 24 and the vinyl system resin of number average molecular weight 15000. The nonvolatile matter of this resin solution was 49%. Hereafter, this is written as a resin solution (A-3).

[0106] <The synthetic example 4> (composition of anionic radical content organic high molecular compounds)

The mixed liquor which consists of the n-butyl methacrylate 175 section, the n-butyl acrylate 10.7 section, the beta-hydroxyethyl methacrylate 37.5 section, the methacrylic-acid 26.8 section, and the "par butyl O"20.0 section was prepared.

[0107] Next, after carrying out a temperature up to 75 degrees C, agitating under a N2 seal after teaching the methyl-ethyl-ketone 250 section to a flask, the above-mentioned mixed liquor was dropped for 2 hours, it was made to react at this temperature further for 15 hours, and the acid number of solid content obtained the solution of 68 and the vinyl system resin of number average molecular weight 5600. The nonvolatile matter of this resin solution was 50%. Hereafter, this is written as a resin solution (A-4).

[0108] <The synthetic example 5> (composition of anionic radical content organic high molecular compounds)

The mixed liquor which consists of the n-butyl methacrylate 153.8 section, the n-butyl acrylate 20.4 section, the beta-hydroxyethyl methacrylate 37.5 section, the methacrylic-acid 38.3 section, and the "par butyl O"5.0 section was prepared. Next, it is [0109] under the N2 seal after teaching the methyl-ethyl-ketone 250 section to a flask. After carrying out a temperature up to 75 degrees C, agitating, the above-mentioned mixed liquor was dropped for 2 hours, it was made to react at this temperature further for 15 hours, and the acid number of solid content obtained the solution of 98 and the vinyl system resin of number average molecular weight 12500. The nonvolatile matter of this resin solution was 51%. Hereafter, this is written as a resin solution (A-5).

[0110] <The synthetic example 6> (composition of anionic radical content organic high molecular compounds)

The mixed liquor which consists of the n-butyl methacrylate 171.4 section, the n-butyl acrylate 6.3 section, the beta-hydroxyethyl methacrylate 37.5 section, the acrylic-acid 34.8 section, and the "par butyl O"20.0 section was prepared.

[0111] Next, after carrying out a temperature up to 75 degrees C, agitating under a N2 seal after teaching the methyl-ethyl-ketone 250 section to a flask, the above-mentioned mixed liquor was dropped for 2 hours, it was made to react at this temperature further for 15 hours, and the acid number of solid content obtained the solution of 95 and the vinyl system resin of number average molecular weight 8800. The nonvolatile matter of this resin solution was 50%. Hereafter, this is written as a resin solution (A-6).

[0112] <The synthetic example 7> (for synthetic - gelation processing of anionic radical content organic high molecular compounds)

The mixed liquor which consists of the n-butyl methacrylate 83.8 section, the n-butyl acrylate 89.4 section, the beta-hydroxyethyl methacrylate 37.5 section, the methacrylic-acid 26.7 section, the glycidyl methacrylate 12.5 section, and the "par butyl O"20.0 section was prepared.

[0113] Next, after carrying out a temperature up to 75 degrees C, agitating under a N2 seal after teaching the methyl-ethyl-ketone 250 section to a flask, the above-mentioned mixed liquor was dropped for 2 hours, it was made to react at this temperature further for 15 hours, and the acid number of solid content obtained the solution of 69 and the vinyl system resin of number average molecular weight 10400. The nonvolatile matter of this resin solution was 50%. Hereafter, this is written as a resin solution (A-7).

[0114]

[Table 1]

	樹脂溶液	分子量	酸価	不揮発分%
合成例 1	A-1	1 2 5 0 0	7 0	4 8
合成例 2	A-2	1 4 0 0 0	4 8	4 9
合成例 3	A-3	1 5 0 0 0	2 4	4 9
合成例 4	A-4	5 6 0 0	6 8	5 0
合成例 5	A-5	1 2 5 0 0	9 8	5 1
合成例 6	A-6	8 8 0 0	9 5	5 0
合成例 7	A-7	1 0 4 0 0	6 9	5 0

[0115] <The example 1 of manufacture> (manufacture of the anionic microencapsulation pigment content aqueous dispersion liquid of a copper copper phthalocyanine blue)

The resin solution (A-5) 22.1 section, "fast gene blue, TGR" (the C.I. pigment blue 15 by Dainippon Ink & Chemicals, Inc., and the mean particle diameter of 50nm) which were obtained in the synthetic example 5 As the maximum particle diameter 14.25 sections of 100nm, and a distributed assistant, the dimethyl aminomethyl copper-phthalocyanine 0.75 section, The methyl-ethyl-ketone 78.2 section, "super BEKKAMIN the L-109-60"(melamine resin by Dainippon Ink & Chemicals, Inc.) 4.7 section, and the ceramic bead 300 section After putting into the container made from stainless steel, the mixture was distributed using the bead mill disperser, and the paste for microencapsulation pigments was prepared.

[0116] Next, irradiating a 45kHz supersonic wave at an organic phase, it was dropped into the organic

phase, having applied [ ion-exchange-water 50 ] it for 12 minutes, self-distribution (phase inversion emulsification) was performed, and anionic microencapsulation pigment content aqueous dispersion liquid were obtained [ after mixing using an agitator after putting the paste 40.0 above-mentioned section for microencapsulation pigments, and the dimethylamino ethanol 0.4 section into Pori Kapp, and considering as an organic phase, while agitating this organic phase, and ].

[0117] Furthermore, after making a solvent distill off by distilling these microencapsulation pigment content aqueous dispersion liquid at 85 degrees C, it held at this temperature for 5 hours, and gelation processing of a capsule wall was performed.

[0118] Thus, as a result of measuring the particle size of the microencapsulation pigment in the obtained anionic microencapsulation pigment content aqueous dispersion liquid (MC-1) using "UPA-150" (laser-doppler method particle-size-distribution measurement machine by Nikkiso Co., Ltd.), the volume mean particle diameter of a microencapsulation pigment was 148nm, and the particle 1000nm or more of the maximum particle diameter was 0%. Moreover, the nonvolatile matter concentration of microencapsulation pigment content aqueous dispersion liquid was 24.5%, and the content of the pigment in a microcapsule was 51.7%.

[0119] <The example 2 of manufacture> (manufacture of the anionic microencapsulation pigment content aqueous dispersion liquid of a copper copper phthalocyanine blue)

(1) After adding zirconia-beads 250g whose mean particle diameter is 0.5mm after adding the resin solution (A-4) 15.0 section, the dimethylethanolamine 0.8 section, and the "fast gene blue and TGR"15 section which were obtained in the synthetic example 4 to a glass bottle with a pigment kneading process capacity of 250ml, adding ion exchange water and making it a total amount become the 75 sections, kneading was performed for 4 hours using the paint shaker. The glass bead was carried out the \*\* exception after kneading termination, and what distributed in water the resin which has the carboxyl group neutralized by the base, and the dispersing element which consists of a pigment was obtained.

[0120] (2) Agitating by DISUPA, after adding water to what distributed in water the resin which has the carboxyl group neutralized by the \*\*\*\* base, and the dispersing element which consists of a pigment and diluting twice, it added until resin insolubilized 1 convention hydrochloric acid and it fixed to the pigment. pH at this time was 3-5.

[0121] (3) The salt was rinsed and the water cake was obtained, after carrying out suction filtration of the aqueous medium containing the pigment which filtration and rinsing resin fixed.

[0122] (4) Agitating neutralization and the re-distribution water cake to an aqueous medium using DISUPA, 10% water solution of dimethylethanolamine was added until pH of a dispersing element was set to 8.5-9.5. Furthermore, after continuing churning for 1 hour, water was added, and it adjusted so that a nonvolatile matter might become 20%, and anionic microencapsulation pigment content aqueous dispersion liquid (MC-2) were obtained.

[0123] As a result of measuring the particle size of the microencapsulation pigment in anionic microencapsulation pigment content aqueous dispersion liquid (MC-2) like the example 1 of manufacture, the volume mean particle diameter of a microencapsulation pigment was 170nm, and the particle 1000nm or more was 0%. Moreover, the content of the pigment in a microcapsule was 67%.

[0124] <The example 3 of manufacture> (manufacture of the anionic microencapsulation pigment content aqueous dispersion liquid of the copper copper phthalocyanine blue by mineral salt)

(1) What distributed in water the resin which has the carboxyl group neutralized by the base like the example 2 of pigment kneading process manufacture, and the dispersing element which consists of a pigment was obtained.

[0125] (2) Agitating by DISUPA, after adding water to what distributed in water the resin which has the carboxyl group neutralized by the \*\*\*\* base, and the dispersing element which consists of a pigment and diluting twice, it added until resin insolubilized 1 convention hydrochloric acid and it fixed to the pigment.

pH at this time was 3-5.

[0126] (3) The salt was rinsed and the water cake was obtained, after carrying out suction filtration of the aqueous medium containing the pigment which filtration and rinsing resin fixed.

[0127] (4) Agitating neutralization and the re-distribution water cake to an aqueous medium using DISUPA, the sodium-hydroxide water solution was added 10% until pH of a dispersing element was set to 8.5-9.5. Furthermore, after continuing churning for 1 hour, water was added, and it adjusted so that a nonvolatile matter might become 20%, and anionic microencapsulation pigment content aqueous dispersion liquid (MC-3) were obtained.

[0128] As a result of measuring the particle size of the microencapsulation pigment in anionic microencapsulation pigment content aqueous dispersion liquid (MC-3) like the example 1 of manufacture, the volume mean particle diameter of a microencapsulation pigment was 182nm, and the particle 1000nm or more was 0%. Moreover, the content of the pigment in a microcapsule was 67%.

[0129] <The example 4 of manufacture> (manufacture of the anionic microencapsulation pigment content aqueous dispersion liquid of a copper copper phthalocyanine blue)

Except having used what neutralized the resin which has a carboxyl group in the resin solution (A-2) obtained in the synthetic example 2 100% using dimethylethanolamine, like the example 2 of manufacture, pigment kneading, \*\*\*\*, filtration and rinsing, neutralization, and re-distribution were performed, and the nonvolatile matter obtained 20% of anionic microencapsulation pigment content aqueous dispersion liquid (MC-4).

[0130] As a result of measuring the particle size of the microencapsulation pigment in anionic microencapsulation pigment content aqueous dispersion liquid (MC-4) like the example 2 of manufacture, the volume mean particle diameter of a microencapsulation pigment was 218nm, and the particle 1000nm or more was 0%. Moreover, the content of the pigment in a microcapsule was 67%.

[0131] <The example 5 of manufacture> (manufacture of the anionic microencapsulation pigment content aqueous dispersion liquid of the copper copper phthalocyanine blue which used the anionic organic high molecular compounds of the acid number 25)

(1) The resin which has a carboxyl group in the resin solution (A-3) obtained in the example 3 of pigment kneading process composition was neutralized 100% using dimethylethanolamine. After adding the methyl ethyl ketone of an amount in which the 7.5 sections and the "fast gene blue and TGR"15 section are added by solid content conversion, and resin dissolves the neutralized resin to a glass bottle with a capacity of 250ml, adding ion exchange water and making it a total amount become the 75 sections, zirconia-beads 250g whose mean particle diameter is 0.5mm was added, and kneading was performed for 4 hours using the paint shaker. The glass bead was carried out the \*\* exception after kneading termination, and what distributed in water the resin which has the carboxyl group neutralized by the base, and the dispersing element which consists of a pigment was obtained.

[0132] (2) Agitating by DISUPA, after adding water to what distributed in water the resin which has the carboxyl group neutralized by the \*\*\*\* base, and the dispersing element which consists of a pigment and diluting twice, it added until resin insolubilized 1 convention hydrochloric acid and it fixed to the pigment. pH at this time was 3-5.

[0133] (3) The salt was rinsed and the water cake was obtained, after carrying out suction filtration of the aqueous medium containing the pigment which filtration and rinsing resin fixed.

[0134] (4) Agitating neutralization and the re-distribution water cake to an aqueous medium using DISUPA, 10% water solution of dimethylethanolamine was added until pH of a dispersing element was set to 8.5-9.5. Furthermore, after continuing churning for 1 hour, water was added, and it adjusted so that a nonvolatile matter might become 20%, and anionic microencapsulation pigment content aqueous dispersion liquid (MC-5) were obtained.

[0135] As a result of measuring the particle size of the microencapsulation pigment in anionic microencapsulation pigment content aqueous dispersion liquid (MC-5) like the example 1 of manufacture,

the volume mean particle diameter of a microencapsulation pigment was 650nm, and the particle 1000nm or more was 17%. Moreover, the content of the pigment in a microcapsule was 67%.

[0136] <The example 6 of manufacture> (manufacture of the anionic microencapsulation pigment content aqueous dispersion liquid of a Magenta color)

The resin solution (A-1) 23.4 section, "a fast gene super Magenta and RTS" (the C.I. pigment red 122 by Dainippon Ink & Chemicals, Inc., and the mean particle diameter of 45nm) which were obtained in the synthetic example 1 As the maximum particle diameter 14.25 sections of 100nm, and a distributed assistant, the dimethyl aminomethyl Quinacridone 0.75 section, The methyl-ethyl-ketone 76.9 section, "super BEKKAMIN the L-109-60"(melamine resin by Dainippon Ink & Chemicals, Inc.) 4.7 section, and the ceramic bead 300 section After putting into the container made from stainless steel, the mixture was distributed using the bead mill disperser, and the paste for microencapsulation pigments was prepared.

[0137] Next, irradiating a 45kHz supersonic wave at an organic phase, it was dropped into the organic phase, having applied [ ion-exchange-water 50 ] it for 12 minutes, self-distribution (phase inversion emulsification) was performed, and anionic microencapsulation pigment content aqueous dispersion liquid were obtained [ after mixing using an agitator after putting the paste 40.0 above-mentioned section for microencapsulation pigments, and the dimethylamino ethanol 0.4 section into Pori Kapp, and considering as an organic phase, while agitating this organic phase, and ].

[0138] Furthermore, after making a solvent distill off by distilling these microencapsulation pigment content aqueous dispersion liquid at 85 degrees C, it held at this temperature for 5 hours, and gelation processing of a capsule wall was performed.

[0139] Thus, as a result of measuring the particle size of the microencapsulation pigment in the obtained anionic microencapsulation pigment content aqueous dispersion liquid (MC-6) like the example 1 of manufacture, the volume mean particle diameter of a microencapsulation pigment was 145nm, and the particle 1000nm or more of the maximum particle diameter was 0%. Moreover, the nonvolatile matter concentration of microencapsulation pigment content aqueous dispersion liquid was 23.2%, and the content of the pigment in a microcapsule was 51.7%.

[0140] <The example 7 of manufacture> (manufacture of the anionic microencapsulation pigment content aqueous dispersion liquid of a Magenta color)

(1) The resin solution (A-4) 15.0 section obtained in the synthetic example 4 to the glass bottle with a pigment kneading process capacity of 250ml, The dimethylethanolamine 0.8 section and "a fast gene super Magenta and RTS" (the C.I. pigment red 122 by Dainippon Ink & Chemicals, Inc., and the mean particle diameter of 45nm) After adding zirconia-beads 250g whose mean particle diameter is 0.5mm after adding the maximum particle diameter 15 sections of 100nm, adding ion exchange water and making it a total amount become the 75 sections, the paint shaker performed kneading for 4 hours. The glass bead was carried out the \*\* exception after kneading termination, and what distributed in water the resin which has the carboxyl group neutralized by the base, and the dispersing element which consists of a pigment was obtained.

[0141] (2) Agitating by DISUPA, after adding water to what distributed in water the resin which has the carboxyl group neutralized by the \*\*\*\* base, and the dispersing element which consists of a pigment and diluting twice, it added until resin insolubilized 1 convention hydrochloric acid and it fixed to the pigment. pH at this time was 3-5.

[0142] (3) The salt was rinsed and the water cake was obtained, after carrying out suction filtration of the aqueous medium containing the pigment which filtration and rinsing resin fixed.

[0143] (4) Agitating neutralization and the re-distribution water cake to an aqueous medium using DISUPA, 10% water solution of dimethylethanolamine was added until pH of a dispersing element was set to 8.5-9.5. Furthermore, after continuing churning for 1 hour, water was added, and it adjusted so that a nonvolatile matter might become 20%, and anionic microencapsulation pigment content aqueous dispersion liquid (MC-7) were obtained.

[0144] As well as the example 1 of manufacture as a result of measuring the particle size of the microencapsulation pigment in anionic microencapsulation pigment content aqueous dispersion liquid (MC-7), the volume mean particle diameter of a microencapsulation pigment was 176nm, and the particle 1000nm or more was 0%. Moreover, the content of the pigment in a microcapsule was 67%.

[0145] <The example 8 of manufacture> (manufacture of the anionic microencapsulation pigment content aqueous dispersion liquid of the Magenta color whose content of an organic pigment is 83%)

In the example 7 of manufacture, except having made into the 6.0 sections the amount of the resin solution (A-4) used at a pigment kneading process, pigment kneading, \*\*\*\*, filtration and rinsing, neutralization, and re-distribution were performed like the example 7 of manufacture, and the nonvolatile matter obtained 20% of anionic microencapsulation pigment content aqueous dispersion liquid (MC-8).

[0146] As a result of measuring the particle size of the microencapsulation pigment in anionic microencapsulation pigment content aqueous dispersion liquid (MC-8) like the example 1 of manufacture, the volume mean particle diameter of a microencapsulation pigment was 250nm, and the particle 1000nm or more was 0%. Moreover, the content of the pigment in a microcapsule was 83%.

[0147] <The example 9 of manufacture> (manufacture of the anionic microencapsulation pigment content aqueous dispersion liquid of the Magenta color whose content of an organic pigment is 75%)

In the example 7 of manufacture, the amount of the resin solution (A-4) used at a pigment kneading process was made into the 10.0 sections, like the example 7 of manufacture, pigment kneading, \*\*\*\*, filtration and rinsing, neutralization, and re-distribution were performed, and the nonvolatile matter obtained 20% of anionic microencapsulation pigment content aqueous dispersion liquid (MC-9) except having used the ethyl ethyl ketone 5.0 section with the resin solution (A-4).

[0148] As a result of measuring the particle size of the microencapsulation pigment in anionic microencapsulation pigment content aqueous dispersion liquid (MC-9) like the example 1 of manufacture, the volume mean particle diameter of a microencapsulation pigment was 180nm, and the particle 1000nm or more was 0%. Moreover, the content of the pigment in a microcapsule was 75%.

[0149] <The example 10 of manufacture> (manufacture of the anionic microencapsulation pigment content aqueous dispersion liquid of the Magenta color whose content of an organic pigment is 33%)

(1) After adding zirconia-beads 250g whose mean particle diameter is 0.5mm after adding the resin solution (A-4) 20.0 section, the dimethylethanolamine 1.1 section, and the fast gene super Magenta and "RTS" 5.0 section which were obtained in the synthetic example 4 to a glass bottle with a pigment-content powder process capacity of 250ml, adding ion exchange water and making it a total amount become the 75 sections, kneading was performed for 4 hours using the paint shaker. The glass bead was carried out the \*\* exception after kneading termination, and what distributed in water the resin which has the carboxyl group neutralized by the base, and the dispersing element which consists of a pigment was obtained.

[0150] Next, like the example 7 of manufacture, \*\*\*\*, filtration and rinsing, neutralization, and re-distribution were performed, and the nonvolatile matter obtained 20% of anionic microencapsulation pigment content aqueous dispersion liquid (MC-10).

[0151] As well as the example 1 of manufacture as a result of measuring the particle size of the microencapsulation pigment in anionic microencapsulation pigment content aqueous dispersion liquid (MC-10), the volume mean particle diameter of a microencapsulation pigment was 224nm, and the particle 1000nm or more was 0%. Moreover, the content of the pigment in a microcapsule was 33%.

[0152] <The example 11 of manufacture> (manufacture of the anionic microencapsulation pigment content aqueous dispersion liquid of the Magenta color which used the organic pigment whose mean particle diameter is 250nm)

It replaces with "a fast gene super Magenta and RTS" in the example 7 of manufacture. Except having used "clo MOFUTARU red and DPP-BO" (the Ciba-Geigy C.I. pigment red 254, mean particle diameter of 250nm, the maximum particle diameter of 400nm) Like the example 7 of manufacture, pigment



kneading, \*\*\*\*, filtration and rinsing, neutralization, and re-distribution were performed, and the nonvolatile matter obtained 20% of anionic microencapsulation pigment content aqueous dispersion liquid (MC-11).

[0153] As well as the example 1 of manufacture as a result of measuring the particle size of the microencapsulation pigment in anionic microencapsulation pigment content aqueous dispersion liquid (MC-11), the volume mean particle diameter of a microencapsulation pigment was 283nm, and the particle 1000nm or more of the maximum particle diameter was 0%. Moreover, the content of the pigment in a microcapsule was 67%.

[0154] <The example 12 of manufacture> (manufacture of the anionic microencapsulation pigment content aqueous dispersion liquid of a yellow color)

The resin solution (A-1) 23.4 section, "SHIMURA fast yellow and 8GTF" (the C.I. pigment yellow 17 by Dainippon Ink & Chemicals, Inc., and the mean particle diameter of 60nm) which were obtained in the synthetic example 1 The maximum particle diameter 15.0 sections of 120nm, the methyl-ethyl-ketone 76.9 section, "super BEKKAMIN the L-109-60"(melamine resin by Dainippon Ink & Chemicals, Inc.) 4.7 section, and the ceramic bead 300 section After putting into the container made from stainless steel, the mixture was distributed using the bead mill disperser, and the paste for microencapsulation pigments was prepared.

[0155] Next, irradiating a 45kHz supersonic wave at an organic phase, it was dropped into the organic phase, having applied [ ion-exchange-water 50 ] it for 12 minutes, self-distribution (phase inversion emulsification) was performed, and anionic microencapsulation pigment content aqueous dispersion liquid were obtained [ after mixing using an agitator after putting the paste 40.0 above-mentioned section for microencapsulation pigments, and the dimethylamino ethanol 0.4 section into Pori Kapp, and considering as an organic phase, while agitating this organic phase, and ].

[0156] Furthermore, after making a solvent distill off by distilling these microencapsulation pigment content aqueous dispersion liquid at 85 degrees C, it held at this temperature for 5 hours, and gelation processing of a capsule wall was performed.

[0157] Thus, as a result of measuring the particle size of the microencapsulation pigment in the obtained anionic microencapsulation pigment content aqueous dispersion liquid (MC-12) like the example 1 of manufacture, the volume mean particle diameter of a microencapsulation pigment was 191nm, and the particle 1000nm or more of the maximum particle diameter was 0%. Moreover, the nonvolatile matter concentration of microencapsulation pigment content aqueous dispersion liquid was 23.8%, and the content of the pigment in a microcapsule was 51.7%.

[0158] <The example 13 of manufacture> (manufacture of the anionic microencapsulation pigment content aqueous dispersion liquid of a yellow color)

(1) After adding zirconia-beads 250g whose mean particle diameter is 0.5mm after adding the resin solution (A-1) 15.6 section, the dimethylethanolamine 0.8 section, and the SHIMURA first yellow and "8GTF" 15 section which were obtained in the synthetic example 1 to a glass bottle with a pigment kneading process capacity of 250ml, adding ion exchange water and making it a total amount become the 75 sections, kneading was performed for 4 hours using the paint shaker. The glass bead was carried out the \*\* exception after kneading termination, and what distributed in water the resin which has the carboxyl group neutralized by the base, and the dispersing element which consists of a pigment was obtained.

[0159] (2) Agitating by DISUPA, after adding water to what distributed in water the resin which has the carboxyl group neutralized by the \*\*\*\* base, and the dispersing element which consists of a pigment and diluting twice, it added until resin insolubilized 1 convention hydrochloric acid and it fixed to the pigment. pH at this time was 3-5.

[0160] (3) The salt was rinsed and the water cake was obtained, after carrying out suction filtration of the aqueous medium containing the pigment which filtration and rinsing resin fixed.

[0161] (4) Agitating neutralization and the re-distribution water cake to an aqueous medium using DISUPA, 10% water solution of dimethylethanolamine was added until pH of a dispersing element was set to 8.5-9.5. Furthermore, after continuing churning for 1 hour, water was added, and it adjusted so that a nonvolatile matter might become 20%, and the anionic microencapsulation pigment content aqueous dispersion liquid (MC-13) of a yellow color were obtained.

[0162] As well as the example 1 of manufacture as a result of measuring the particle size of the microencapsulation pigment in anionic microencapsulation pigment content aqueous dispersion liquid (MC-13), the volume mean particle diameter of a microencapsulation pigment was 183nm, and the particle 1000nm or more was 0%. Moreover, the content of the pigment in a microcapsule was 67%.

[0163] <The example 14 of manufacture> (manufacture of the anionic microencapsulation pigment content aqueous dispersion liquid of the yellow color which used the organic pigment whose mean particle diameter is 220nm)

It replaces with "SHIMURA fast yellow and 8GTF" in the example 13 of manufacture. It is made to be the same as that of the example 13 of manufacture except having used "SHIMURA fast yellow and 4192" (the C.I. pigment yellow 154 by Dainippon Ink & Chemicals, Inc., mean particle diameter of 220nm, the maximum particle diameter of 350nm). Pigment kneading, \*\*\*\*, filtration and rinsing, neutralization, and re-distribution were performed, and the nonvolatile matter obtained 20% of anionic microencapsulation pigment content aqueous dispersion liquid (MC-14).

[0164] As well as the example 1 of manufacture as a result of measuring the particle size of the microencapsulation pigment in anionic microencapsulation pigment content aqueous dispersion liquid (MC-14), the volume mean particle diameter of a microencapsulation pigment was 245nm, and the particle 1000nm or more was 0%. Moreover, the content of the pigment in a microcapsule was 67%.

[0165] <The example 15 of manufacture> (manufacture of the anionic microencapsulation pigment content aqueous dispersion liquid of the cyanogen color which used the base of a non-volatile)

(1) After adding zirconia-beads 250g whose mean particle diameter is 0.5mm after adding the resin solution (A-6) 15.0 section, the dimethylethanolamine 1.1 section, and the "fast gene blue and TGR" 15 section which were obtained in the synthetic example 6 to a glass bottle with a pigment kneading process capacity of 250ml, adding ion exchange water and making it a total amount become the 75 sections, kneading was performed for 4 hours using the paint shaker. The glass bead was carried out the \*\* exception after kneading termination, and what distributed in water the resin which has the carboxyl group neutralized by the base, and the dispersing element which consists of a pigment was obtained.

[0166] (2) Agitating by DISUPA, after adding water to what distributed in water the resin which has the carboxyl group neutralized by the \*\*\*\* base, and the dispersing element which consists of a pigment and diluting twice, it added until resin insolubilized 1 convention hydrochloric acid and it fixed to the pigment. pH at this time was 3-5.

[0167] (3) The salt was rinsed and the water cake was obtained, after carrying out suction filtration of the aqueous medium containing the pigment which filtration and rinsing resin fixed.

[0168] (4) Agitating neutralization and the re-distribution water cake to an aqueous medium using DISUPA, the sodium-hydroxide water solution was added 10% until pH of a dispersing element was set to 8.5-9.5. Furthermore, after continuing churning for 1 hour, water was added, and it adjusted so that a nonvolatile matter might become 20%, and the anionic microencapsulation pigment content aqueous dispersion liquid (MC-15) of a blue color were obtained.

[0169] As well as the example 1 of manufacture as a result of measuring the particle size of the microencapsulation pigment in anionic microencapsulation pigment content aqueous dispersion liquid (MC-15), the volume mean particle diameter of a microencapsulation pigment was 152nm, and the particle 1000nm or more was 0%. Moreover, the content of the pigment in a microcapsule was 67%.

[0170] <The example 16 of manufacture> (manufacture of the anionic microencapsulation pigment

content aqueous dispersion liquid of the Magenta color which used the base of a non-volatile)  
 It replaces with "fast gene blue and TGR" in the example 15 of manufacture. Except having replaced with 10% sodium-hydroxide water solution further for neutralization, and having used the potassium-hydroxide water solution 10% using "a fast gene super Magenta and RTS" Like the example 15 of manufacture, pigment kneading, \*\*\*\*, filtration and rinsing, neutralization, and re-distribution were performed, and the nonvolatile matter obtained 20% of anionic microencapsulation pigment content aqueous dispersion liquid (MC-16).

[0171] As well as the example 1 of manufacture as a result of measuring the particle size of the microencapsulation pigment in anionic microencapsulation pigment content aqueous dispersion liquid (MC-16), the volume mean particle diameter of a microencapsulation pigment was 178nm, and the particle 1000nm or more was 0%. Moreover, the content of the pigment in a microcapsule was 67%.

[0172] <The example 17 of manufacture> (manufacture of the anionic microencapsulation pigment content aqueous dispersion liquid of the yellow color which used the base of a non-volatile)

In the example 15 of manufacture, it replaced with "fast gene blue and TGR", and using "SHIMURA fast yellow and 8GTF", like the example 15 of manufacture, pigment kneading, \*\*\*\*, filtration and rinsing, neutralization, and re-distribution were performed, and the nonvolatile matter obtained 20% of anionic microencapsulation pigment content aqueous dispersion liquid (MC-17) except having replaced with 10% sodium-hydroxide water solution further for neutralization, and having used the lithium-hydroxide water solution 10%.

[0173] As well as the example 1 of manufacture as a result of measuring the particle size of the microencapsulation pigment in anionic microencapsulation pigment content aqueous dispersion liquid (MC-17), the volume mean particle diameter of a microencapsulation pigment was 182nm, and the particle 1000nm or more was 0%. Moreover, the content of the pigment in a microcapsule was 67%.

[0174] <The example 18 of manufacture> (manufacture of the anionic microencapsulation pigment content aqueous dispersion liquid of the carbon black which carried out gelation processing of a capsule wall)

(1) After adding the zirconia-beads 250 section whose mean particle diameter is 0.5mm after adding the resin solution (A-7) 15.0 section, the dimethylethanolamine 0.8 section, and the "MA-600 (Mitsubishi Chemical middle-class carbon black: mean particle diameter of 18nm)" 15 section which were obtained in the synthetic example 7 to a glass bottle with a pigment kneading process capacity of 250ml, adding ion exchange water and making it a total amount become the 75 sections, kneading was performed for 4 hours using the paint shaker. The glass bead was carried out the \*\* exception after kneading termination, and what distributed in water the resin which has the carboxyl group neutralized by the base, and the dispersing element which consists of a pigment was obtained.

[0175] (2) After adding water to what distributed in water the resin which has the carboxyl group neutralized by the gelation processing base, and the dispersing element which consists of a pigment and diluting 3 times, heating gelation processing was carried out at 120 degrees C in the autoclave.

[0176] (3) It added after carrying out \*\*\*\* gelation processing until resin insolubilized 1 convention hydrochloric acid and it fixed to the pigment in ordinary temperature, agitating by DISUPA. pH at this time was 3-5.

[0177] (4) The salt was rinsed and the water cake was obtained, after carrying out suction filtration of the aqueous medium containing the pigment which filtration and rinsing resin fixed.

[0178] (5) Agitating neutralization and the re-distribution water cake to an aqueous medium using DISUPA, the dimethylamino ethanol water solution was added 10% until pH of a dispersing element was set to 8.5-9.5. Furthermore, after continuing churning for 1 hour, water was added, and it adjusted so that a nonvolatile matter might become 20%, and the anionic microencapsulation pigment content aqueous dispersion liquid (MC-18) of carbon black were obtained.

[0179] As well as the example 1 of manufacture as a result of measuring the particle size of the

microencapsulation pigment in anionic microencapsulation pigment content aqueous dispersion liquid (MC-18), the volume mean particle diameter of a microencapsulation pigment was 149nm, and the particle 1000nm or more was 0%. Moreover, the content of the pigment in a microcapsule was 67%.

[0180]

[Table 2]

	樹脂溶液	顔 料	方法	7ミシ	粒子径	N. V.	粗粒	顔料分
製造例 1	A - 5	TGR	転相	DMAE	148nm	24.5%	0%	51.7%
製造例 2	A - 4	TGR	酸析	DMAE	170nm	20%	0%	67%
製造例 3	A - 4	TGR	酸析	NaOH	182nm	20%	0%	67%
製造例 4	A - 2	TGR	酸析	DMAE	218nm	20%	0%	67%
製造例 5	A - 3	TGR	酸析	DMAE	650nm	20%	17%	67%
製造例 6	A - 1	RTS	転相	DMAE	145nm	23.2%	0%	51.7%
製造例 7	A - 4	RTS	酸析	DMAE	176nm	20%	0%	67%
製造例 8	A - 4	RTS	酸析	DMAE	250nm	20%	0%	83%
製造例 9	A - 4	RTS	酸析	DMAE	180nm	20%	0%	75%
製造例10	A - 4	RTS	酸析	DMAE	224nm	20%	0%	33%

[0181]

[Table 3]

	樹脂溶液	顔 料	方法	7ミシ	粒子径	N. V.	粗粒	顔料分
製造例11	A - 4	DPP	酸析	DMAE	283nm	20%	0%	67%
製造例12	A - 1	8GTF	転相	DMAE	191nm	23.8%	0%	51.7%
製造例13	A - 1	8GTF	酸析	DMAE	183nm	20%	0%	67%
製造例14	A - 1	4192	酸析	DMAE	245nm	20%	0%	67%
製造例15	A - 6	TGR	酸析	NaOH	152nm	20%	0%	67%
製造例16	A - 6	RTS	酸析	KOH	178nm	20%	0%	67%
製造例17	A - 6	8GTF	酸析	LiOH	178nm	20%	0%	67%
製造例18	A - 7	C B	酸析	DMAE	149nm	20%	0%	67%

[0182] The cable address in Table 2 and 3 is as follows.

TGR : "fast gene blue and TGR" (C.I. pigment blue 15 by Dainippon Ink & Chemicals, Inc.)

RTS : "a fast gene super Magenta and RTS" (C.I. pigment red 122 by Dainippon Ink & Chemicals, Inc.)

DPP : "clo MOFUTARU red and DPP-BO" (Ciba-Geigy C.I. pigment red 254)

8GTF: "SHIMURA fast yellow and 8GTF" (C.I. pigment yellow 17 by Dainippon Ink & Chemicals, Inc.)

4192: "SHIMURA fast yellow, 4192" (C.I. pigment yellow 154 by Dainippon Ink & Chemicals, Inc.)

CB : carbon black DMAE:dimethylamino ethanol particle diameter : Volume mean-particle-diameter N.V. of a microencapsulation pigment: Nonvolatile matter concentration coarse grain : Rate pigment content of a particle with a particle size [ of a microencapsulation pigment ] of 1000nm or more : Content rate of the pigment in a microcapsule [0183] <Example 1> (manufacture of the recording ink which used the microencapsulation pigment dispersion liquid whose pigment content in a microencapsulation pigment is 67%)

In the anionic microencapsulation pigment content aqueous dispersion-liquid (MC-2) 37.5 section of the copper phthalocyanine blue obtained in the example 2 of manufacture, the ethylene glycol 7.5 section, the glycerol 5.0 section, the diethylene-glycol monobutyl ether 0.5 section, the ethylene-glycol-monomethyl-ether 15.0 section, the isopropyl alcohol 3.0 section, the diethanolamine 3.0 section, and the ion-exchange-water 28.5 section were mixed, and the pigment content prepared the recording ink of 5.0% of cyanogen color in it.

[0184] <Example 2> (manufacture of the recording ink which used the microencapsulation pigment dispersion liquid whose pigment content in a microencapsulation pigment is 67%)

In the example 1, it replaced with the anionic microencapsulation pigment content aqueous dispersion liquid (MC-2) of the copper phthalocyanine blue obtained in the example 2 of manufacture, and the recording ink of a Magenta color was prepared like the example 1 except having used the anionic microencapsulation pigment content aqueous dispersion liquid (MC-7) of the Magenta color obtained in the example 7 of manufacture.

[0185] <Example 3> (manufacture of the recording ink which used the microencapsulation pigment dispersion liquid whose pigment content in a microencapsulation pigment is 67%)

In the example 1, it replaced with the anionic microencapsulation pigment content aqueous dispersion liquid (MC-2) of the copper phthalocyanine blue obtained in the example 2 of manufacture, and the recording ink of a yellow color was prepared like the example 1 except having used the anionic microencapsulation pigment content aqueous dispersion liquid (MC-13) of the yellow color obtained in the example 13 of manufacture.

[0186] In examples 1, 2, and 3, since in preparing recording ink dispersers, such as a bead mill and a roll, were not needed but it prepared only by only mixing especially, while a distributed facility is unnecessary, can shorten a distributed process and an effort, being able to perform compaction of production time, or laborsaving of distributed energy and raising productivity greatly, a manufacturing cost is reducible. Moreover, the pigment content in aqueous dispersion liquid was also as high as 13.4% or more, the pigment content in an anionic microencapsulation pigment is as high as 67%, and versatility was [ the anionic microencapsulation pigment content aqueous dispersion liquid used for these could add other ingredients, such as water soluble resin used in order to improve the engine performance as recording ink, and a water-soluble organic solvent in most amount, and ] high [ dispersion liquid ].

[0187] Next, the volume mean particle diameter after storing at a room temperature, and the sedimentation nature of a particle were shown in Table 4 for the volume mean particle diameter of the microencapsulation pigment in the recording ink of these cyanogen color, a Magenta color, and a yellow color, and 30 days. It is before and after storage, an almost equivalent value is shown, and sedimentation of a particle is not seen further, but it is clear volume mean particle diameter's of the anionic microencapsulation pigment in each recording ink obtained in the examples 1, 2, and 3 to excel in storage stability and distributed stability very much compared with the conventional microencapsulation pigment.

[0188] Next, the color record image of a cyanogen color, a Magenta color, and a yellow color was recorded on an OHP sheet and copy paper using the printer of commercial Bubble Jet using the above-mentioned recording ink. As shown in Table 6, this record image had definition and the high depth of shade, and they were excellent in color rendering properties or transparency. Moreover, since the

image recorded on the OHP sheet was excellent in transparency, it showed colorful projection drawing. It did not disappear, even if it attached water and ground the record image on an OHP sheet, and it excelled also in the water resisting property. Moreover, even if it used it repeatedly, the nozzle which makes ink breathe out was not got blocked.

[0189] <The example 1 of a comparison> (manufacture of the recording ink with which the mean particle diameter of a microencapsulation pigment used the microencapsulation pigment dispersion liquid to which the maximum particle diameter exceeds 1000nm by 650nm)

In the example 1, it replaced with the anionic microencapsulation pigment content aqueosity dispersion liquid (MC-2) of the copper phthalocyanine blue obtained in the example 2 of manufacture, and the recording ink of a cyanogen color was prepared like the example 1 except having used the anionic microencapsulation pigment content aqueosity dispersion liquid (MC-5) of the copper phthalocyanine blue obtained in the example 5 of manufacture.

[0190] The volume mean particle diameter after storing at a room temperature, and the sedimentation nature of a particle were shown in Table 8 for the volume mean particle diameter of the microencapsulation pigment in the recording ink of the cyanogen color obtained in the example 1 of a comparison, and 30 days. Although the volume mean particle diameter of the anionic microencapsulation pigment in the recording ink of this example of a comparison is before and after storage and showed the almost equivalent value, sedimentation of a particle was seen and its distributed stability was bad.

[0191] Next, the color record image of a cyanogen color was recorded on an OHP sheet and copy paper using the commercial bubble-jet printer using the above-mentioned recording ink. As shown in Table 9, this record image had definition and the low depth of shade, and they lacked in color rendering properties or transparency. Moreover, the image recorded on the OHP sheet did not show opaque and colorful projection drawing, and was not able to use it for the OHP sheet. Moreover, while using it repeatedly, the nozzle which makes ink breathe out was got blocked and use of a printer became impossible.

[0192] <Example 4> (manufacture of the recording ink which used the microencapsulation pigment dispersion liquid whose pigment content in a microencapsulation pigment is 51.7%)

In the anionic microencapsulation pigment content aqueosity dispersion-liquid (MC-1) 47.4 section of the copper phthalocyanine blue obtained in the example 1 of manufacture, the ethylene glycol 20 section, the diethanolamine 3.0 section, and the ion-exchange-water 29.6 section were mixed, and the pigment content prepared the recording ink of 6% of cyanogen color in it.

[0193] <Example 5> (manufacture of the recording ink which used the microencapsulation pigment dispersion liquid whose pigment content in a microencapsulation pigment is 51.7%)

In the anionic microencapsulation pigment content aqueosity dispersion-liquid (MC-6) 50.0 section of the Magenta color obtained in the example 6 of manufacture, the ethylene glycol 20 section, the diethanolamine 3.0 section, and the ion-exchange-water 27.0 section were mixed, and the pigment content prepared the recording ink of 6% of Magenta color in it.

[0194] <Example 6> (manufacture of the recording ink which used the microencapsulation pigment dispersion liquid whose pigment content in a microencapsulation pigment is 51.7%)

In the anionic microencapsulation pigment content aqueosity dispersion-liquid (MC-12) 48.8 section of the yellow color obtained in the example 12 of manufacture, the ethylene glycol 20 section, the diethanolamine 3.0 section, and the ion-exchange-water 28.2 section were mixed, and the pigment content prepared the recording ink of 6% of yellow color in it.

[0195] In these examples 4, 5, and 6, since in preparing recording ink dispersers, such as a bead mill and a roll, were not needed but it prepared only by only mixing especially, while a distributed facility is unnecessary, can shorten a distributed process and an effort, being able to perform compaction of production time, or laborsaving of distributed energy and raising productivity greatly, a manufacturing

cost is reducible. Moreover, the pigment content in aqueous dispersion liquid was also as high as 10% or more, the pigment content in an anionic microencapsulation pigment is as high as 51.7%, and versatility was [ the anionic microencapsulation pigment content aqueous dispersion liquid used for these could add other ingredients, such as a water-soluble organic solvent used in order to improve the engine performance as recording ink, in most amount, and ] high [ dispersion liquid ].

[0196] The volume mean particle diameter after storing at a room temperature, and the sedimentation nature of a particle were shown in Table 4 for the volume mean particle diameter of the microencapsulation pigment in the recording ink of these cyanogen color, a Magenta color, and a yellow color, and 30 days. It is before and after storage, an almost equivalent value is shown, and sedimentation of a particle is not seen further, but it is clear volume mean particle diameter's of the anionic microencapsulation pigment in the recording ink of this example to excel in storage stability and distributed stability very much compared with the conventional microencapsulation pigment.

[0197] Next, the color record image of a cyanogen color, a Magenta color, and a yellow color was recorded on an OHP sheet and copy paper using the ink jet printer of a commercial piezo method using the above-mentioned recording ink. As shown in Table 6, this record image had definition and the high depth of shade, and they were excellent in color rendering properties or transparency. Moreover, since the image recorded on the OHP sheet was excellent in transparency, it showed colorful projection drawing. It did not disappear, even if it attached water and ground the record image on an OHP sheet, and it excelled also in the water resisting property. Moreover, even if it used it repeatedly, the nozzle which makes ink breathe out was not got blocked.

[0198] <Example 7> (manufacture of the recording ink which used the microencapsulation pigment dispersion liquid whose pigment content in a microencapsulation pigment is 67%)

In the anionic microencapsulation pigment content aqueous dispersion-liquid (MC-2) 44.8 section of the copper phthalocyanine blue obtained in the example 2 of manufacture, the aqueous ammonia solution 5.0 section (equivalent to the resin solid content 2.5 section) of styrene acrylic acid resin of 50% of nonvolatile matters of the acid number 163 and molecular weight 25,000, the ethylene glycol 20 section, the diethanolamine 3.0 section, and the ion-exchange-water 27.2 section were mixed, and the pigment content prepared the recording ink of 6% of cyanogen color in it.

[0199] <Example 8> (manufacture of the recording ink which used the microencapsulation pigment dispersion liquid whose pigment content in a microencapsulation pigment is 67%)

In the example 7, it replaced with the anionic microencapsulation pigment content aqueous dispersion liquid (MC-2) of the copper phthalocyanine blue obtained in the example 2 of manufacture, and the recording ink of a Magenta color was prepared like the example 7 except having used the anionic microencapsulation pigment content aqueous dispersion liquid (MC-7) of the Magenta color obtained in the example 7 of manufacture.

[0200] <Example 9> (manufacture of the recording ink which used the microencapsulation pigment dispersion liquid whose pigment content in a microencapsulation pigment is 67%)

In the example 7, it replaced with the anionic microencapsulation pigment content aqueous dispersion liquid (MC-2) of the copper phthalocyanine blue obtained in the example 2 of manufacture, and the recording ink of a yellow color was prepared like the example 7 except having used the anionic microencapsulation pigment content aqueous dispersion liquid (MC-13) of the yellow color obtained in the example 13 of manufacture.

[0201] <Example 10> (manufacture of the recording ink which used the microencapsulation pigment dispersion liquid whose pigment content in a microencapsulation pigment is 75%)

The aqueous ammonia solution 5.0 section (equivalent to the resin solid content 2.5 section) of the styrene acrylic acid resin used for the anionic microencapsulation pigment content aqueous dispersion-liquid (MC-9) 40.0 section of the Magenta color obtained in the example 9 of manufacture in the example 7, the ethylene glycol 20 section, the diethanolamine 3.0 section, and the



ion-exchange-water 32.0 section were mixed, and the pigment content prepared the recording ink of 6% of Magenta color.

[0202] <Example 11> (manufacture of the recording ink which used the microencapsulation pigment dispersion liquid whose pigment content in a microencapsulation pigment is 67%)

In the example 7, it replaced with the anionic microencapsulation pigment content aqueous dispersion liquid (MC-2) of the copper phthalocyanine blue obtained in the example 2 of manufacture, and the recording ink of a cyanogen color was prepared like the example 7 except having used the anionic microencapsulation pigment content aqueous dispersion liquid (MC-4) of the copper phthalocyanine blue obtained in the example 4 of manufacture.

[0203] In examples 7, 8, 9, 10, and 11, since in preparing recording ink dispersers, such as a bead mill and a roll, were not needed but it prepared only by only mixing especially, while a distributed facility is unnecessary, can shorten a distributed process and an effort, being able to perform compaction of production time, or laborsaving of distributed energy and raising productivity greatly, a manufacturing cost is reducible. Moreover, the pigment content in aqueous dispersion liquid was also as high as 13.4% or more, the pigment content in an anionic microencapsulation pigment is as high as 67% or more, and versatility was [ the anionic microencapsulation pigment content aqueous dispersion liquid used for these could add other ingredients, such as water soluble resin used in order to improve the engine performance as recording ink, and a water-soluble organic solvent, in most amount, and ] high [ dispersion liquid ].

[0204] The volume mean particle diameter after storing at a room temperature, and the sedimentation nature of a particle were shown in Table 5 for the volume mean particle diameter of the microencapsulation pigment in the recording ink of these cyanogen color, a Magenta color, and a yellow color, and 30 days. It is before and after storage, an almost equivalent value is shown, and sedimentation of a particle is not seen further, but it is clear volume mean particle diameter's of the anionic microencapsulation pigment in the recording ink of this example to excel in storage stability and distributed stability very much compared with the conventional microencapsulation pigment.

[0205] Next, the color record image of a cyanogen color, a Magenta color, and a yellow color was recorded on an OHP sheet and copy paper using the ink jet printer of a commercial piezo method using the above-mentioned recording ink. As shown in Tables 6 and 7, this record image had definition and the high depth of shade, and they were excellent in color rendering properties or transparency. Moreover, since the image recorded on the OHP sheet was excellent in transparency, it showed colorful projection drawing. It did not disappear, even if it attached water and ground the record image on an OHP sheet, and it excelled also in the water resisting property. Moreover, even if it used it repeatedly, the nozzle which makes ink breathe out was not got blocked.

[0206] <The example 2 of a comparison> (manufacture of the recording ink which used the microencapsulation pigment dispersion liquid whose pigment content in a microencapsulation pigment is 33%)

The aqueous ammonia solution 5.0 section (equivalent to the resin solid content 2.5 section) of the styrene acrylic acid resin used for the anionic microencapsulation pigment content aqueous dispersion-liquid (MC-10) 90.1 section of the Magenta color obtained in the example 10 of manufacture in the example 7, the ethylene glycol 1.9 section, and the diethanolamine 3.0 section were mixed, and the pigment content prepared the recording ink of 6% of Magenta color.

[0207] The anionic microencapsulation pigment content aqueous dispersion liquid used for this had the pigment content as low as 33% in an anionic microencapsulation pigment, and its pigment content in aqueous dispersion liquid was also as low as 6.6%, and they were what a limitation is in the addition of other ingredients, such as water soluble resin used in order to improve the engine performance as recording ink, and a water-soluble organic solvent, with the depth of shade of recording ink maintained, and lacks in versatility. Moreover, since there were many amounts of resin used for a microcapsule, the

problem arose in compatibility with other ingredients.

[0208] The volume mean particle diameter after storing at a room temperature, and the sedimentation nature of a particle were shown in Table 8 for the volume mean particle diameter of the microencapsulation pigment in the recording ink of this Magenta color, and 30 days. It is before and after storage, the almost equivalent value was shown, and sedimentation of a particle was not seen further, but the volume mean particle diameter of the anionic microencapsulation pigment in the recording ink of this example of a comparison was very excellent in storage stability and distributed stability.

[0209] Next, the color record image of a Magenta color was recorded on an OHP sheet and copy paper using the ink jet printer of a commercial piezo method using the above-mentioned recording ink. Since there were few additions of the ethylene glycol in recording ink, it produced a blot and flipping to copy paper or an OHP sheet, and as the record image was shown in Table 9, definition was low and color rendering properties and transparency were missing. Moreover, the image recorded on the OHP sheet did not show opaque and colorful projection drawing, and was not able to use it for the OHP sheet. It did not disappear, even if it attached water and ground the record image on an OHP sheet, and it excelled in the water resisting property. Moreover, when it was used repeatedly, the nozzle which makes ink breathe out might be got blocked.

[0210] <The example 3 of a comparison> (manufacture of the recording ink which used the microencapsulation pigment dispersion liquid whose pigment content in a microencapsulation pigment is 83%)

The aqueous ammonia solution 5.0 section (equivalent to the resin solid content 2.5 section) of the styrene acrylic acid resin used for the anionic microencapsulation pigment content aqueous dispersion-liquid (MC-8) 36.1 section of the Magenta color obtained in the example 8 of manufacture in the example 7, the ethylene glycol 20 section, the diethanolamine 3.0 section, and the ion-exchange-water 35.9 section were mixed, and the pigment content prepared the recording ink of 6% of Magenta color.

[0211] The volume mean particle diameter after storing at a room temperature, and the sedimentation nature of a particle were shown in Table 8 for the volume mean particle diameter of the microencapsulation pigment in the recording ink of this Magenta color, and 30 days. Since the anionic microencapsulation pigment in the recording ink of this example of a comparison had low resin concentration, a pigment was not made as for things to maintaining at stability in the detailed condition, but a lifting and volume mean particle diameter became large about the condensation after storage, sedimentation of a particle was also seen, and the anionic microencapsulation pigment had storage stability and bad distributed stability.

[0212] Next, the color record image of a Magenta color was recorded on an OHP sheet and copy paper using the ink jet printer of a commercial piezo method using the above-mentioned recording ink. Since the capsule had caused condensation, as shown in Table 9, this record image had definition and the low depth of shade, and they lacked in color rendering properties or transparency. Moreover, the image recorded on the OHP sheet did not show opaque and colorful projection drawing, and was not able to use it for the OHP sheet. Moreover, while using it repeatedly, the nozzle which makes ink breathe out was got blocked and use of a printer became impossible.

[0213] <The example 4 of a comparison> (manufacture of the recording ink with which the mean particle diameter of a microencapsulation pigment used the microencapsulation pigment dispersion liquid to which the maximum particle diameter exceeds 1000nm by 650nm)

The aqueous ammonia solution 5.0 section (equivalent to the resin solid content 2.5 section) of the styrene acrylic acid resin used for the anionic microencapsulation pigment content aqueous dispersion-liquid (MC-5) 44.8 section of the copper phthalocyanine blue obtained in the example 5 of manufacture in the example 7, the ethylene glycol 20 section, the diethanolamine 3.0 section, and the ion-exchange-water 27.2 section were mixed, and the pigment content prepared the recording ink of 6%

of cyanogen color.

[0214] The volume mean particle diameter after storing at a room temperature, and the sedimentation nature of a particle were shown in Table 8 for the volume mean particle diameter of the microencapsulation pigment in the recording ink of this cyanogen color, and 30 days. Although the volume mean particle diameter of the anionic microencapsulation pigment in the recording ink of this example of a comparison is before and after storage and showed the almost equivalent value, sedimentation of a particle was seen and storage stability and its distributed stability were bad.

[0215] Next, the color record image of a cyanogen color was recorded on an OHP sheet and copy paper using the ink jet printer of a commercial piezo method using the above-mentioned recording ink. As shown in Table 9, this record image had definition and the low depth of shade, and they lacked in color rendering properties or transparency. Moreover, the image recorded on the OHP sheet did not show opaque and colorful projection drawing, and was not able to use it for the OHP sheet. Moreover, while using it repeatedly, the nozzle which makes ink breathe out was got blocked and use of a printer became impossible.

[0216] <The example 5 of a comparison> (manufacture of the recording ink which used the microencapsulation pigment dispersion liquid to which the mean particle diameter of an organic pigment exceeds 200nm)

The aqueous ammonia solution 5.0 section (equivalent to the resin solid content 2.5 section) of the styrene acrylic acid resin used for the anionic microencapsulation pigment content aqueous dispersion-liquid (MC-11) 44.8 section of the Magenta color obtained in the example 11 of manufacture in the example 7, the ethylene glycol 20 section, the diethanolamine 3.0 section, and the ion-exchange-water 27.2 section were mixed, and the pigment content prepared the recording ink of 6% of Magenta color.

[0217] The volume mean particle diameter after storing at a room temperature, and the sedimentation nature of a particle were shown in Table 8 for the volume mean particle diameter of the microencapsulation pigment in the recording ink of this Magenta color, and 30 days. It is before and after storage, the almost equivalent value was shown, and sedimentation of a particle was not seen, but the volume mean particle diameter of the anionic microencapsulation pigment in the recording ink of this example of a comparison was excellent in storage stability and distributed stability.

[0218] Next, the color record image of a Magenta color was recorded on an OHP sheet and copy paper using the ink jet printer of a commercial piezo method using the above-mentioned recording ink. As shown in Table 9, this record image had definition and the low depth of shade, and they lacked in color rendering properties or transparency. Especially the image recorded on the OHP sheet did not show opaque and colorful projection drawing, and was not able to use it for the OHP sheet. Moreover, even if it used it repeatedly, the nozzle which makes ink breathe out was not got blocked.

[0219] <The example 6 of a comparison> (manufacture of the recording ink which used the microencapsulation pigment dispersion liquid to which the mean particle diameter of an organic pigment exceeds 200nm)

The aqueous ammonia solution 5.0 section (equivalent to the resin solid content 2.5 section) of the styrene acrylic acid resin used for the anionic microencapsulation pigment content aqueous dispersion-liquid (MC-14) 44.8 section of the yellow color obtained in the example 14 of manufacture in the example 7, the ethylene glycol 20 section, the JIETANORU amine 3.0 section, and the ion-exchange-water 27.2 section were mixed, and the pigment content prepared the recording ink of 6% of yellow color.

[0220] The volume mean particle diameter after storing at a room temperature, and the sedimentation nature of a particle were shown in Table 8 for the volume mean particle diameter of the microencapsulation pigment in the recording ink of this yellow color, and 30 days. It is before and after storage, the almost equivalent value was shown, and sedimentation of a particle was not seen, but the

volume mean particle diameter of the anionic microencapsulation pigment in the recording ink of this example of a comparison was excellent in storage stability and distributed stability.

[0221] Next, the color record image of a Magenta color was recorded on an OHP sheet and copy paper using the ink jet printer of a commercial piezo method using the above-mentioned recording ink. As shown in Table 9, this record image had definition and the low depth of shade, and they lacked in color rendering properties or transparency. Especially the image recorded on the OHP sheet did not show opaque and colorful projection drawing, and was not able to use it for the OHP sheet. Moreover, even if it used it repeatedly, the nozzle which makes ink breathe out was not got blocked.

[0222] <Example 12> (manufacture of the recording ink which used the microencapsulation pigment dispersion liquid of the base of a non-volatile)

In the anionic microencapsulation pigment content aqueous dispersion-liquid (MC-15) 37.5 section of the copper phthalocyanine blue obtained in the example 15 of manufacture, the ethylene glycol 5 section, the glycerol 10.0 section, the diethanolamine 3.0 section, and the ion-exchange-water 44.5 section were mixed, and the pigment content prepared the recording ink of 5.0% of cyanogen color in it.

[0223] <Example 13> (manufacture of the recording ink which used the microencapsulation pigment dispersion liquid of the base of a non-volatile)

In the example 12, it replaced with the anionic microencapsulation pigment content aqueous dispersion liquid (MC-15) of the copper phthalocyanine blue obtained in the example 15 of manufacture, and the recording ink of a Magenta color was prepared like the example 12 except having used the anionic microencapsulation pigment content aqueous dispersion liquid (MC-16) of the Magenta color obtained in the example 16 of manufacture.

[0224] <Example 14> (manufacture of the recording ink which used the microencapsulation pigment dispersion liquid of the base of a non-volatile)

In the example 12, it replaced with the anionic microencapsulation pigment content aqueous dispersion liquid (MC-15) of the copper phthalocyanine blue obtained in the example 15 of manufacture, and the recording ink of a yellow color was prepared like the example 12 except having used the anionic microencapsulation pigment content aqueous dispersion liquid (MC-17) of the yellow color obtained in the example 17 of manufacture.

[0225] In examples 12, 13, and 14, since in preparing recording ink dispersers, such as a bead mill and a roll, were not needed but it prepared only by only mixing especially, while a distributed facility is unnecessary, can shorten a distributed process and an effort, being able to perform compaction of production time, or laborsaving of distributed energy and raising productivity greatly, a manufacturing cost is reducible. Moreover, the pigment content in aqueous dispersion liquid was also as high as 13.4% or more, the pigment content in an anionic microencapsulation pigment is as high as 67%, and versatility was [ the anionic microencapsulation pigment content aqueous dispersion liquid used for these could add other ingredients, such as water soluble resin used in order to improve the engine performance as recording ink, and a water-soluble organic solvent in most amount, and ] high [ dispersion liquid ].

[0226] Next, the volume mean particle diameter after storing at a room temperature, and the sedimentation nature of a particle were shown in Table 5 for the volume mean particle diameter of the microencapsulation pigment in the recording ink of these cyanogen color, a Magenta color, and a yellow color, and 30 days. It is before and after storage, an almost equivalent value is shown, and sedimentation of a particle is not seen further, but it is clear volume mean particle diameter's of the anionic microencapsulation pigment in each recording ink obtained in the examples 12, 13, and 14 to excel in storage stability and distributed stability very much compared with the conventional microencapsulation pigment.

[0227] Next, the color record image of a cyanogen color, a Magenta color, and a yellow color was recorded on an OHP sheet and copy paper using the printer of a commercial piezo method using the above-mentioned recording ink. As shown in Table 7, these record images had definition and the high

depth of shade, and they were excellent in color rendering properties or transparency. Moreover, since this record image was excellent in transparency, it showed colorful projection drawing. Furthermore, when water was attached and the record image on an OHP sheet was **\*\***(ed), it was easy to disappear, but even if it hung down several drops of water to the record image in the copy paper, it spread, a record image did not disappear and it excelled also in the water resisting property.

[0228] Moreover, since the count of cleaning was managed with less than 3 times compared with the case where an volatile amine is used when it was cleaned and used after leaving the nozzle which packed the ink of these cyanogen colors, a Magenta color, and a yellow color for 15 days at a room temperature, it excelled in redispersible [ of ink ] very much.

[0229] <Example 15> (manufacture of the recording ink which used the microencapsulation pigment dispersion liquid which carried out gelation processing)

In the anionic microencapsulation pigment content aqueosity dispersion-liquid (MC-18) 37.5 section of the carbon black obtained in the example 18 of manufacture, the ethylene glycol 5 section, the glycerol 10.0 section, the diethanolamine 3.0 section, and the ion-exchange-water 44.5 section were mixed, and the pigment content prepared the recording ink of 5.0% of carbon black in it.

[0230] Next, the volume mean particle diameter after storing at a room temperature, and the sedimentation nature of a particle were shown in Table 5 for the volume mean particle diameter of the microencapsulation pigment in the recording ink of this carbon black, and 30 days. It is before and after storage, an almost equivalent value is shown, and sedimentation of a particle is not seen further, but it is clear volume mean particle diameter's of the anionic microencapsulation pigment in this recording ink to excel in storage stability and distributed stability very much compared with the conventional microencapsulation pigment.

[0231] Next, the record image of a BURRAKU color was recorded on an OHP sheet and copy paper using the ink jet printer of a commercial piezo method using the above-mentioned recording ink. As shown in Table 7, these record images had a Japanese lacquer black tint, and definition and its depth of shade were high. Furthermore, it was it hard to disappear to attach water and to **\*\*** the record image on an OHP sheet, and excelled also in the water resisting property.

[0232] Moreover, when it was cleaned and used after leaving the nozzle which packed this recording ink for 15 days at a room temperature, since the count of cleaning was managed with 6 times, it excelled also in redispersible [ of ink ].

[0233] Furthermore, when this recording ink was put into the glass bottle, and was sealed and the thermostat performed the resistance to solvents test for ten days at 80 degrees C, it excelled very much, without volume mean particle diameter being changeless and condensing compared with 189nm and trial before.

[0234] <Example 16> (manufacture of the recording ink which used the microencapsulation pigment dispersion liquid of the base of a non-volatile)

The aqueous ammonia solution 5.0 section (equivalent to the resin solid content 2.5 section) of the styrene acrylic acid resin used for the anionic microencapsulation pigment content aqueosity dispersion-liquid (MC-3) 44.8 section of the copper phthalocyanine blue obtained in the example 3 of manufacture in the example 7, the ethylene glycol 20 section, the diethanolamine 3.0 section, and the ion-exchange-water 27.2 section were mixed, and the pigment content prepared the recording ink of 6% of cyanogen color.

[0235] The volume mean particle diameter after storing at a room temperature, and the sedimentation nature of a particle were shown in Table 5 for the volume mean particle diameter of the microencapsulation pigment in the recording ink of this cyanogen color, and 30 days. It is before and after storage, the almost equivalent value was shown, and sedimentation of a particle was not seen, but the volume mean particle diameter of the anionic microencapsulation pigment in the recording ink of this example of a comparison was excellent in storage stability and distributed stability.

[0236] Next, the color record image of a cyanogen color was recorded on an OHP sheet and copy paper using the ink jet printer of a commercial piezo method using the above-mentioned recording ink. As shown in Table 7, this record image had definition and the high depth of shade, and they were excellent in color rendering properties or transparency. Projection drawing transparent [ especially the image recorded on the OHP sheet ] and colorful was shown. Furthermore, when water was attached and the record image on an OHP sheet was \*\* (ed), it was easy to disappear, but even if it hung down several drops of water to the record image in the copy paper, it spread, a record image did not disappear and it excelled also in the water resisting property.

[0237] Moreover, when it was cleaned and used after leaving the nozzle which packed the recording ink of this cyanogen color for 15 days at a room temperature, since the count of cleaning was managed with less than 3 times, it excelled in redispersible [ of ink ] very much.

[0238]

[Table 4]

	マイクロカプセル化顔料含有水性分散液	体積平均径 (nm)		沈降性
		貯蔵前	貯蔵後	
実施例 1	MC-2	175	180	○
実施例 2	MC-7	182	186	○
実施例 3	MC-13	192	190	○
実施例 4	MC-1	152	155	○
実施例 5	MC-6	143	148	○
実施例 6	MC-12	182	179	○
実施例 7	MC-2	176	183	○
実施例 8	MC-7	173	172	○
実施例 9	MC-13	183	192	○
実施例 10	MC-9	185	189	○

[0239]

[Table 5]

	マイクロカプセル化顔料含有水性分散液	体積平均径 (nm)		沈降性
		貯蔵前	貯蔵後	
実施例11	MC-4	225	221	○
実施例12	MC-15	158	154	○
実施例13	MC-16	182	174	○
実施例14	MC-17	188	193	○
実施例15	MC-18	153	147	○
実施例16	MC-3	172	171	○

[0240] The cable address in Tables 4 and 5, the evaluation approach, and the valuation basis are as follows.

Volume mean diameter : volume mean particle diameter of an anionic microencapsulation pigment (nm)

Sedimentation nature : [0241] as which sedimentation condition O= fitness x= sedimentation of the particle after storage is regarded

[Table 6]

	マイクロカプセル化顔料含有水性分散液	ジェットプリンタの種類	再分散性	記録画像			
				耐水性	精細度	色濃度	透明性
実施例1	MC-2	BJ	—	○	○	○	○
実施例2	MC-7	BJ	—	○	○	○	○
実施例3	MC-13	BJ	—	○	○	○	○
実施例4	MC-1	PJ	△	○	○	○	○
実施例5	MC-6	PJ	△	○	○	○	○
実施例6	MC-12	PJ	△	○	○	○	○
実施例7	MC-2	PJ	△	○	○	○	○
実施例8	MC-7	PJ	△	○	○	○	○
実施例9	MC-13	PJ	△	○	○	○	○
実施例10	MC-9	PJ	△	○	○	○	○

[0242]

[Table 7]



	マイクロカプセル化顔料含有水性分散液	ジェットプリンタの種類	再分散性	記録画像			
				耐水性	精細度	色濃度	透明性
実施例11	MC-4	PJ	△	○	○	○	○
実施例12	MC-15	PJ	○	△	○	○	○
実施例13	MC-16	PJ	○	△	○	○	○
実施例14	MC-17	PJ	○	△	○	○	○
実施例15	MC-18	PJ	△	○	○	○	-
実施例16	MC-3	PJ	○	△	○	○	○

[0243] The cable address in Tables 6 and 7, the evaluation approach, and the valuation basis are as follows.

BJ : ink jet printer of Bubble Jet PJ : Ink jet printer of a piezo method Redispersible : While it had been filled up with ink, it prints again after leaving it in mesoeium for 15 days at a room temperature, and easy estimates.

O = cleaning is printable within 3 times. \*\* = cleaning 4 - 9 times More than x=10 time - : Un-evaluating. Water resisting property : An O=OHP sheet does not disappear, either. In \*\* = copy paper, a blot [ little ] It permeates in x= copy paper and a record image cannot be read. Definition : O= fitness x = it is bad. Depth of shade : O = it is high. x = it is low. Transparency : O= transparence x= opacity [0244]

[Table 8]

	マイクロカプセル化顔料含有水性分散液	体積平均径(nm)		沈降性
		貯蔵前	貯蔵後	
比較例1	MC-5	570	581	×
比較例2	MC-7	230	235	○
比較例3	MC-13	735	1259	×
比較例4	MC-5	690	770	×
比較例5	MC-1	290	307	○
比較例6	MC-6	257	265	○

[0245] The cable address in Table 8, the evaluation approach, and the valuation basis are as follows.

Volume mean diameter : volume mean particle diameter of an anionic microencapsulation pigment (nm)

Sedimentation nature : [0246] as which sedimentation condition O= fitness x= sedimentation of the particle after storage is regarded

[Table 9]

	マイクロ カプセル 化顔料 含有水性 分散液	ジェット プリンタ の種類	再 分 散 性	記 録 画 像			
				耐 水 性	精 細 度	色 濃 度	透 明 性
比較例 1	MC-5	BJ	-	-	×	×	×
比較例 2	MC-10	PJ	-	○	×	×	×
比較例 3	MC-8	PJ	-	-	×	×	×
比較例 4	MC-5	PJ	-	-	×	×	×
比較例 5	MC-11	PJ	-	-	×	×	×
比較例 6	MC-14	PJ	-	-	×	×	×

[0247] The cable address in Table 9, the evaluation approach, and the valuation basis are as follows.

BJ : ink jet printer of Bubble Jet PJ : Ink jet printer of a piezo method Redispersible : While it had been filled up with ink, it prints again after leaving it in mesoecium for 15 days at a room temperature, and easy estimates.

O = cleaning is printable within 3 times. \*\* = cleaning 4 - 9 times More than x=10 time - : un-evaluating. Water resisting property : An O=OHP sheet does not disappear, either. In \*\* = copy paper, a blot [ little ] It permeates in x= copy paper and a record image cannot be read. Definition : O = good x = it is bad. Depth of shade : O = it is high. x = it is low. Transparency : O = transparence x = opaque

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[Claim(s)]

[Claim 1]

the recording ink characterized by being in the range the organic pigment in an anionic microencapsulation pigment or whose content rate of carbon black it is anionic microencapsulation pigment content aqueous dispersion liquid which cover an organic pigment or carbon black with anionic radical content organic high molecular compounds, and change, and is 35 - 80 % of the weight -- service water -- sex dispersion liquid.

[Claim 2]

Aqueous dispersion liquid for recording ink according to claim 1 whose mean particle diameter the maximum particle diameter of an anionic microencapsulation pigment is 1000nm or less, and is 300nm or less.

[Claim 3]

Aqueous dispersion liquid for recording ink according to claim 1 or 2 characterized by for the maximum particle diameter being 200nm or less, and being an anionic microencapsulation pigment containing the organic pigment or carbon black in the range whose mean particle diameter of a primary particle is 10-100nm.

[Claim 4]

Aqueous dispersion liquid for recording ink according to claim 1, 2, or 3 characterized by containing the anionic microencapsulation pigment which covered the curing agent and/or the high molecular compound, and the organic pigment with anionic radical content organic high molecular compounds.

[Claim 5]

Aqueous dispersion liquid for recording ink according to claim 1, 2, or 3 using the anionic microencapsulation pigment obtained by throwing water into the organic solvent phase containing anionic radical content organic high molecular compounds and an organic pigment, or carbon black.

[Claim 6]

Aqueous dispersion liquid for recording ink according to claim 4 using the anionic microencapsulation pigment obtained by throwing water into the organic solvent phase containing anionic radical content organic high molecular compounds, an organic pigment or carbon black and a curing agent, and/or a high molecular compound.

[Claim 7]

Aqueous dispersion liquid for recording ink according to claim 5 or 6 using the anionic microencapsulation pigment obtained by throwing in water, irradiating a supersonic wave at the organic solvent phase containing anionic radical content organic high molecular compounds and an organic pigment, or carbon black.

[Claim 8]

Aqueous dispersion liquid for recording ink according to claim 1, 2, or 3 using the anionic microencapsulation pigment obtained by supplying the organic solvent phase containing anionic radical content organic high molecular compounds and an organic pigment, or carbon black underwater.

[Claim 9]

Aqueous dispersion liquid for recording ink according to claim 4 using the anionic microencapsulation pigment obtained by supplying the organic solvent phase containing anionic radical content organic high molecular compounds, an organic pigment or carbon black and a curing agent, and/or a high molecular compound underwater.

[Claim 10]

Aqueous dispersion liquid for recording ink according to claim 1, 2, 3, or 4 using the anionic microencapsulation pigment obtained by neutralizing all the anionic all [ a part or ] using a basic

compound in the water cake which consists of anionic radical content organic high molecular compounds and an organic pigment, or carbon black.

[Claim 11]

Aquosity dispersion liquid for recording ink according to claim 8 or 9 which use the water cake obtained by the process which neutralizes that a basic compound is also in all the anionic all [ a part or ] of anionic radical content organic high molecular compounds, and consists of a process kneaded an organic pigment or carbon black, and in an aquosity medium, and a process which pH is carried out to an acid compound being at neutrality or acidity, and anionic radical content organic high molecular compounds are deposited, and fixes to a pigment.

[Claim 12]

Recording ink containing the aquosity dispersion liquid for recording ink according to claim 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, or 11.

[Claim 13]

Recording ink according to claim 12 which is an object for ink jet printers.

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